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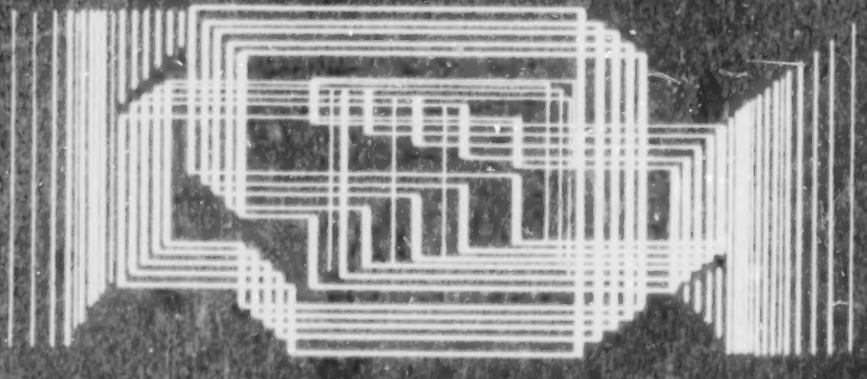
DYNAMIC IRRADIATION CHAMBER TESTS OF AUTOMOTIVE EXHAUST



U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

DYNAMIC IRRADIATION CHAMBER TESTS OF AUTOMOTIVE EXHAUST

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Air Pollution
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FOREWORD

The problem of vehicle exhaust as an air pollutant has been under intensive study by government and private research agencies for several years. Basic to these studies is the determination of the types of pollutants contained in vehicular exhaust, the photochemical reactions that occur when exhaust is discharged into the atmosphere, and the products responsible for various air pollution effects.

Photochemical reactions are being studied in ail by the use of 'smog' chambers, in which vehicular exhaust diluted with air is irradiated to simulate the effects of sunlight in the atmosphere. This report describes irradiation chamber tests conducted by the Division of Air Pollution of the Public Health Service. The work is performed by personnel of the Division's Laboratory of Engineering and Physical Sciences at the Robert A. Taft Sanitary Engineering Center.

Preliminary tests were conducted at the Center beginning in February 1960. The dynamic irradiation tests described in this report cover the period from November 1960 to May 1961. This work represents one of a series of irradiation studies whose primary object is the determination of photochemical reactions under a selected variety of laboratory conditions representative of urban atmospheres. Future reports will describe additional test projects, all of which are part of the over-all Public Health Service program of research in environmental health.

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ABSTRACT

As part of an intensive study by government and private agencies the U. S. Public Health Service has built an irradiation chamber facility for investigation of irradiated auto exhaust under mixing conditions similar to those in the atmosphere. The facility consists of a programmed continuous-cycling chassis dynamometer, an exhaust dilution system, a dilution-air purification system, two irradiation chambers, and exposure facilities for evaluation of bacteria kill, plant damage, and various effects on small animals.

Of the three variables studied during the first test series, the exhaust concentration at the start of irradiation appeared to produce the most significant effects. Fuel composition had a lesser influence. Very little difference was noted in the effects produced at two different average irradiation times.

DYNAMIC IRRADIATION CHAMBER TESTS OF AUTOMOTIVE EXHAUST

SUMMARY

A dynamic irradiation chamber facility was designed and built for investigations of irradiated auto exhaust under conditions of continuous mixing. The facility consists of a programmed chassis dynamometer, an exhaust dilution system, a dilution-air purification system, two irradiation chambers, and various exposure facilities.

Three variables were considered in this first series of tests: (1) initial exhaust concentration (approximately 13 ppm carbon and 35 ppm carbon), (2) average irradiation time (85 and 120 minutes), and (3) fuel composition (14% and 23% olefins). The effects of varying these test parameters were determined by use of appropriate test criteria including NO_2 formation rate, oxidant production, total hydrocarbon losses and reaction of specific species, aldehyde production, plant damage, and bacteria kill.

Of the three variables studied, the exhaust concentration at the start of irradiation appeared to produce the most significant effects. Fuel composition had a lesser influence on some of the test criteria; very little difference was noted in the effects produced at the two average irradiation times.

INTRODUCTION

Air masses over urban areas continually undergo varying degrees of mixing of new pollutants with existing pollutants. The degree of mixing depends on atmospheric turbulence and the location and movement of parcels of air with respect to pollutant sources. For study of the atmospheric photochemical oxidation of dilute automotive exhaust under conditions that simulate continuous uniform atmospheric mixing of new with

old pollutants, a dynamic irradiation system has been developed. In this dynamic system, dilute non-irradiated exhaust is continually introduced into the irradiation chamber and dilute irradiated exhaust is continually withdrawn.

TEST FACILITY AND PROCEDURES

The test facility used in this study consists of five major components: an automatically cycled chassis dynamometer to control the production of exhaust gases under simulated driving conditions, a two-stage exhaust-transfer and dilution system to dilute the raw exhaust gases to the specified concentrations, a dilution-air purification system, dynamic irradiation chambers for the irradiation of the dilute exhaust gases, and various exposure facilities (Figure 1; See also Figures 2-5, 8, 9).

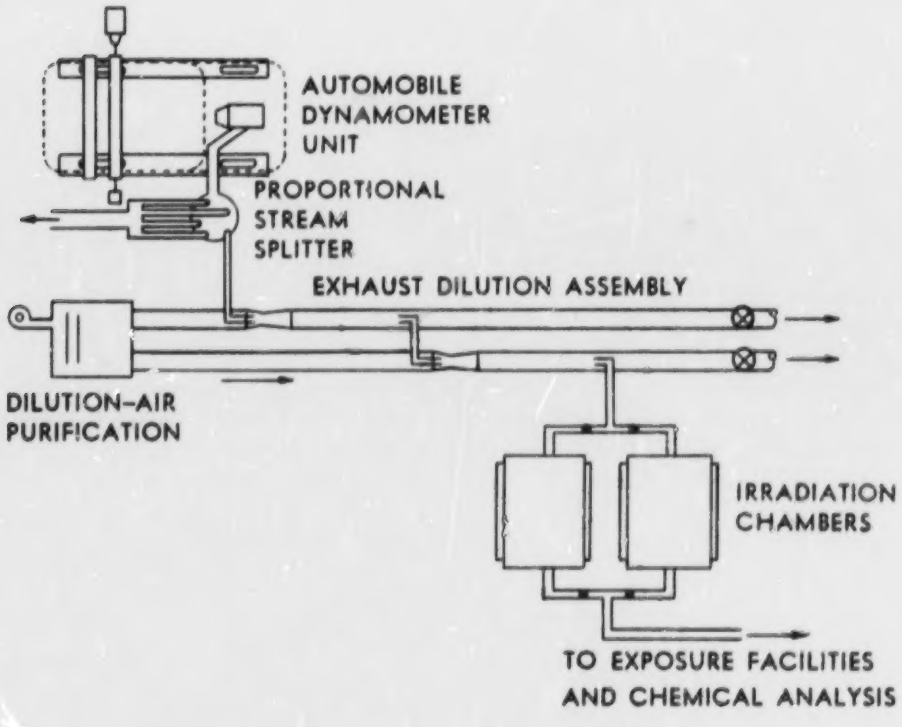

Figure 1. Auto exhaust irradiation facility.

Facility and Procedures

DYNAMOMETER SYSTEM AND TEST ENGINE

To achieve reproducibility of engine operating conditions and hence of exhaust composition for a 10-hour period (the normal period required for dynamic irradiation chamber runs), a controlled hydraulic-type chassis dynamometer was used with the test vehicle engine (Figure 2).

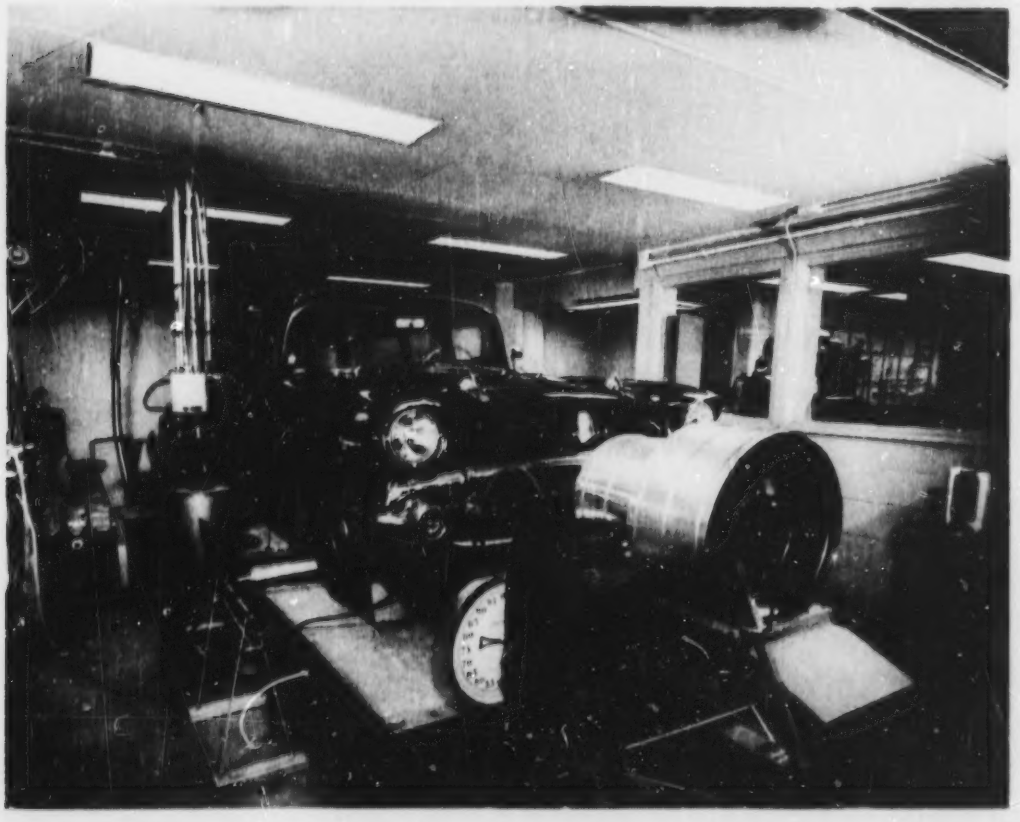

Figure 2. Dynamometer with test vehicle.

To assure that dynamometer operation would simulate actual road conditions, the dynamometer was modified to allow simulation not only of acceleration, uphill driving, and cruise, in which the engine powers the vehicle (engine-load), but also of deceleration and downhill driving, in which the inertia of the vehicle drives the engine (engine-driven). The modification entailed coupling a slave-engine assembly through an overrunning clutch to the power absorption roll to allow contolled motoring

for the engine-driven condition. Horsepower absorption, preset on the dynamometer, established the engine-load conditions. Deviations in dynamometer power absorption and slave-engine power input are on the order of 1.0%. To provide a continuous, rapid, and reproducing cycle for the test vehicle, a programming device for control of the output of the test vehicle engine and the slave engine was necessary. The device that was developed utilized a cam-operated servo mechanism, which controlled throttle position for both the test vehicle engine and the slave engine. Dynamometer horsepower absorption was preset prior to each test run.

The test vehicle was a 1957 six-cylinder Chevrolet station wagon. Measurements of engine speed, manifold vacuum, carburetor air flow, and throttle position, made on the test vehicle during actual road operations, were used as the basis for establishing the power requirements for the programming cycle. Time distribution for the programming cycle was based on the frequency distribution of engine modes reported in earlier studies.[1] The programming cycle thus developed produced exhaust with a ratio of hydrocarbons to oxides of nitrogen of approximately 12:1 (hydrocarbons expressed as ppm total carbon). Following is the sequence of engine conditions.

Condition	Vehicle Speed, mph	Time, min	Manifold Vacuum, in. Hg	Power, hp
Engine-load	18	2.2	18.3	2.0
Engine-driven	24	1.1	23.5	
Engine-load	38	2.2	15.5	9.5
Engine-driven	33	1.1	24.5	
Engine-load	36	2.2	16.0	8.0
Engine-driven	29	1.1	24.0	

Idle mixture in the carburetor was adjusted daily to compensate for the day-to-day variations in exhaust emissions. The ignition system was checked weekly to assure peak condition of the spark plugs and distributor points.

EXHAUST TRANSFER AND DILUTION SYSTEM

The exhaust gases generated by the vehicle on the dynamometer were transferred to the irradiation chambers through the dilution system by means of a proportional stream-splitter, which separated a constant proportion (approximately 20%) of the total exhaust flow (Figure 3). It was required that the sample and waste gas streams discharge to equal pressure zones, and that the pressure drop be identical through both the sample and

waste exhaust gas lines. Since the dilution-air system operated at a positive pressure and since the waste portion of the auto exhaust was discharged to atmosphere, it was necessary to provide a point of essentially atmospheric pressure for introduction of the exhaust sample into the dilution-air system. This was done by introducing the exhaust sample into the primary dilution stage at a venturi throat held at atmospheric pressure.

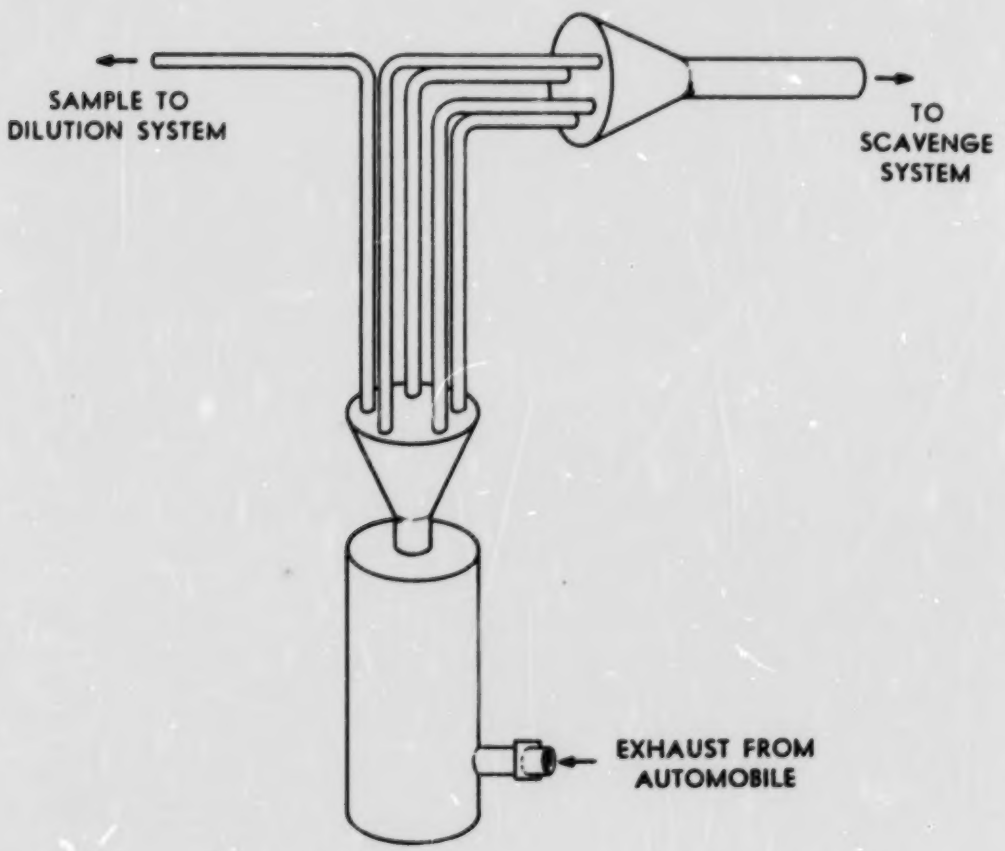

Figure 3. Proportional stream-splitter.

Dilution ratios of 400:1 to 1400:1 were used to establish the hydrocarbon concentrations in the irradiation chamber at the levels designated for irradiation studies. To meet these conditions, the dilution system was constructed as a two-stage unit, with each stage capable of operating at flow rates of 100 to 250 cubic feet per minute. For this series of tests, dilution in the first stage was held constant at ratios of 19:1 to 21:1 while the second-stage dilution was maintained at 18:1 (for high concentration of exhaust) and at 66:1 (for simulated atmospheric concentrations).

To prevent contamination of the dilute automotive exhaust with unfiltered air, the dilution air was supplied under sufficient positive pressure to move the gases through the dilution system, the irradiation chamber, and the exposure facilities. Movement of the exhaust gases at relatively low pressure into the first stage of the dilution system, which was nominally at higher pressure, and transfer of the required portion of the gases from the first dilution stage to the second dilution stage were accomplished by introducing the gas into zones of low pressure created at venturi throats. Rapid mixing also was accomplished by the high velocity and turbulence created by introduction at each venturi throat.

DILUTION-AIR PURIFICATION SYSTEM

The dilution air, with which the exhaust sample is mixed before it is introduced into the irradiation chamber, should be as free as possible of contaminants that would interfere with the photochemical reactions within the chamber. The temperature and humidity of this air should approximately duplicate those conditions found in typical urban atmospheres.

To achieve these conditions, the dilution air was passed through an air conditioning system, which included particulate removal and charcoal filters, a cooling and dehumidifying coil, a heating coil, and a humidifier (Figure 4).

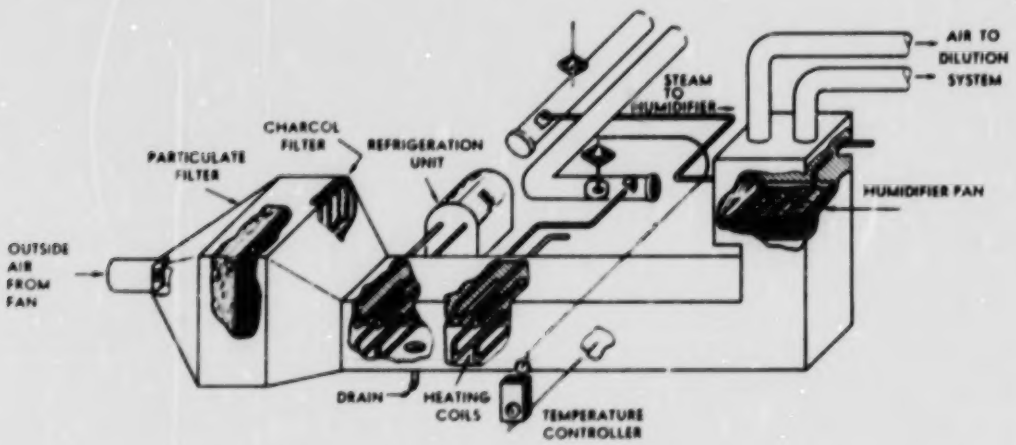

Figure 4. Dilution-air purification system.

The particulate filter was a Cambridge Model ID-1000 absolute filter with 1000-cfm capacity. This filter has an efficiency of 99.95% with 0.3-micron particles. The charcoal filter was a Barneby-Cheyney Model 7-FM cell charged with 45 pounds of activated charcoal. Periodic sampling has shown that a relatively constant hydrocarbon content of less than 2 ppm carbon, which is essentially methane, remains in the clean air.

A 7-1/2-ton-capacity mechanical refrigeration system provided dehumidification and cooling. This system, together with steam heating coils and a steam-heated humidifier, maintained the diluting air at 75°F ± 3°F and 50% ± 5% relative humidity.

IRRADIATION CHAMBERS

Two 335-cubic-foot chambers were constructed for the dynamic irradiation facility. The chambers were designed to operate as ideal dilution volumes into which the raw exhaust gases, diluted to the designated concentration, were continuously introduced as an equal quantity of irradiated gases was withdrawn. The chambers were constructed of aluminum with Mylar windows to allow for the irradiation of the dilute chamber gases (Figure 5).

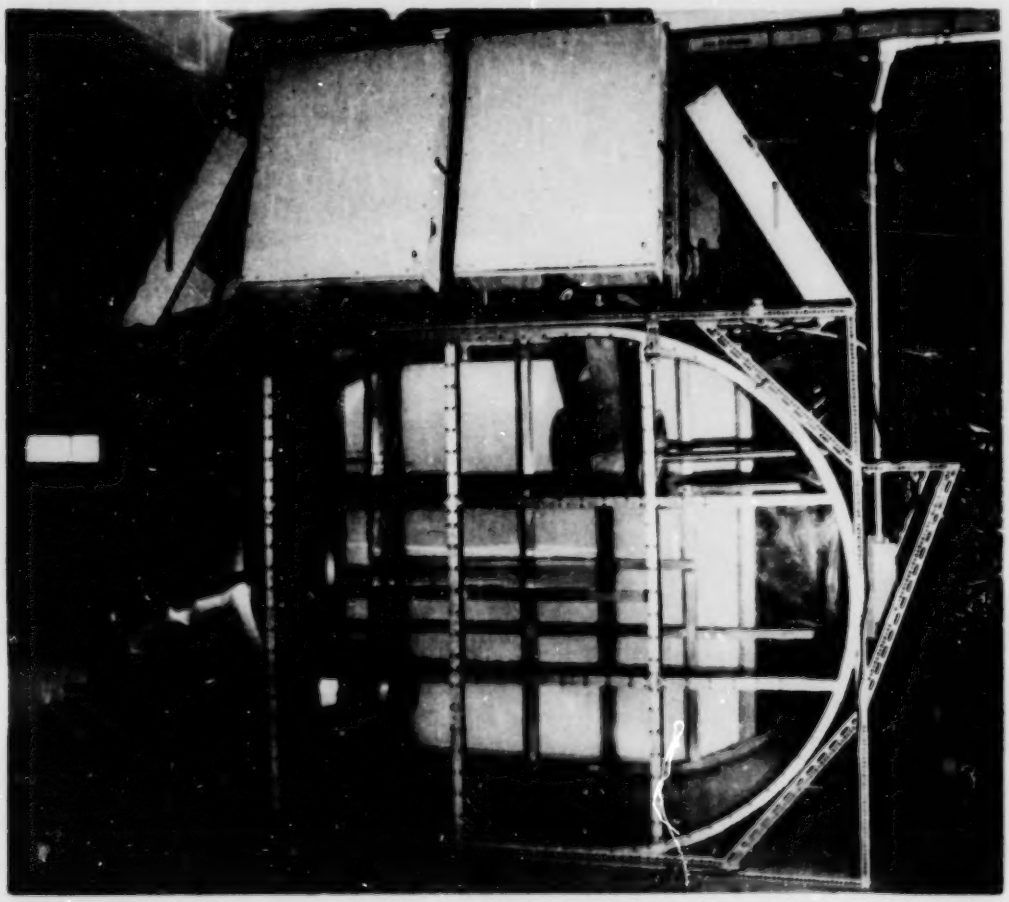

Figure 5. Irradiation chamber.

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IRRADIATION CHAMBER TESTS

For this test series, rapid mixing, necessary for the dynamic chamber to perform as an ideal dilution volume, was produced in each chamber by the jet action of two tube-axial fans, which caused approximately 50% of the gas at the fan to be accelerated ahead and mixed, under turbulent conditions, within the chamber. Since chamber operation approached the performance of an ideal dilution volume, any element of input gas was rapidly and completely mixed into the entire chamber volume and any element of the output gas was representative of the entire volume. Under such conditions the average irradiation time for all molecules of gas in the chamber was equal to:

$$T_a = \frac{1}{k} (1 - e^{-kt}) \qquad (1)$$

Where: T_a = average irradiation time (exposure time)

$k = \frac{q}{v}$

q = chamber flow rate

v = chamber volume

t = time after irradiation begins

The exposure time is therefore determined only by the flow rate through the chamber and the time since start of irradiation.

Irradiation of the gas within the chamber was supplied by illumination from sources external to the chamber through windows of 3-mil-thick Type D Mylar. The illumination was provided by two banks of 70 fluorescent tubes each, mounted in two cavity reflectors. The 96-inch T-8 tubes were operated on T-12 ballasts, which supplied a 25% overload to increase the incident irradiation intensity. Two types of tubes, black light and warm white deluxe, were used in equal proportions to approximate solar radiation between the solar cut-off (about 2900 angstroms) and 3700 angstroms. The choice of Mylar as window material was a compromise among many factors, including spectral transmission, strength, surface adsorption, and diffusion. Strength and surface characteristics of the Mylar were found to be adequate. As shown in Figure 6, the spectral transmission curve for the Mylar is smooth, with a cut-off point between 3100 and 3200 angstroms, which is somewhat higher than the solar cut-off. The spectral distribution and intensity in the near-ultraviolet range produced in the chamber, as shown in Figure 7, approximated that of noonday sunlight[2] below 3700 angstroms.

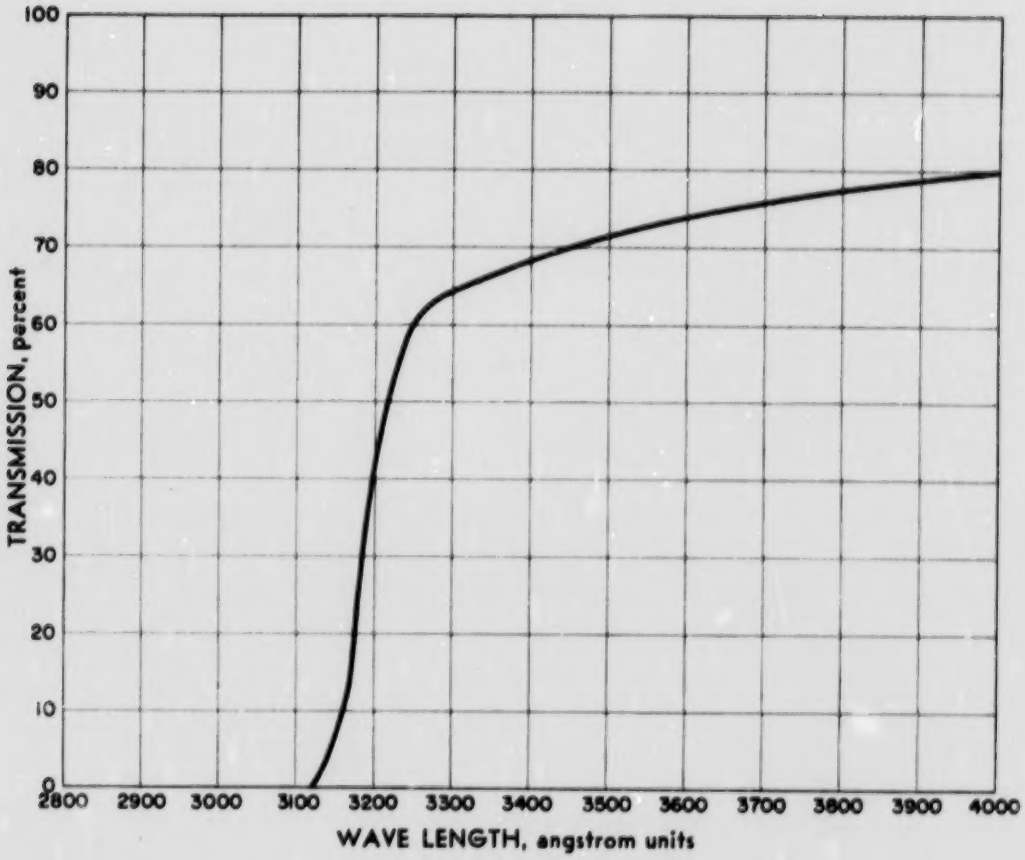

Figure 6. Spectral transmission curve for 3-mil Mylar.

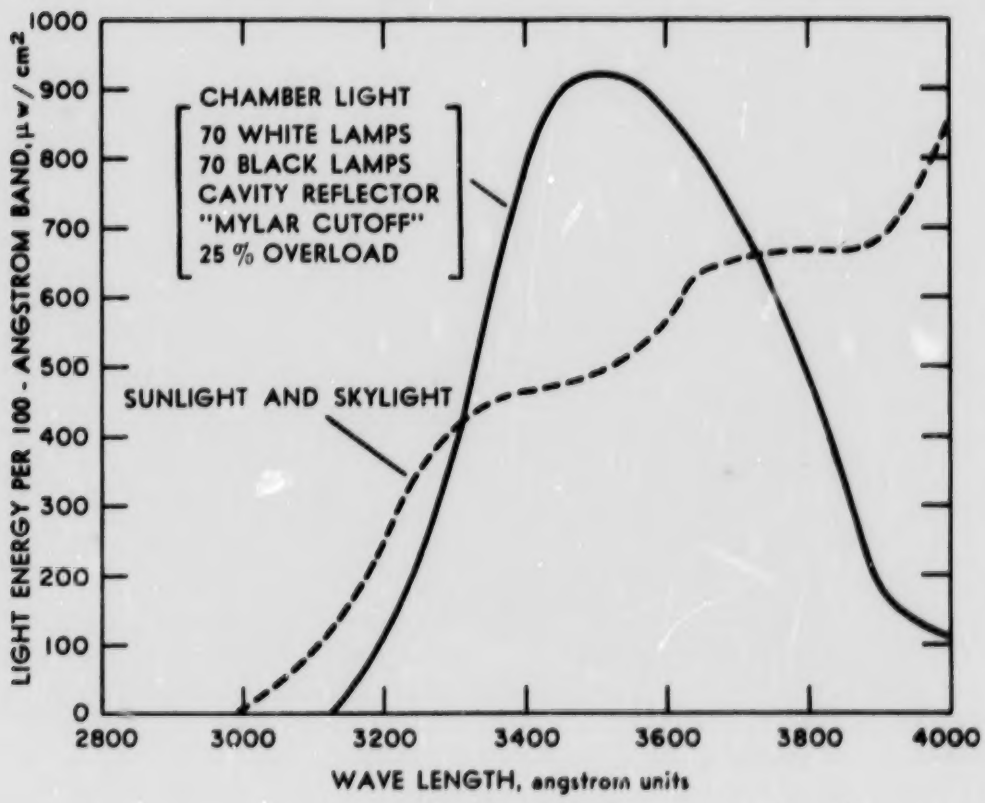

Figure 7. Light intensity.

To minimize surface effects, the chamber was made as large as possible within laboratory space limitations to reduce the surface-to-volume ratio. The interior surface was comprised of approximately 168 square feet of Mylar and 132 square feet of aluminum; the surface-to-volume ratio for Mylar was 0.50 and for aluminum, 0.39. These materials have been found to have minimal effect on the major components present in the exhaust gases or produced in the irradiated gases.[3]

The diluted exhaust gases were continuously fed to the dynamic chamber through the inlet port located at the rear of the lower recirculating fan. Simultaneously the irradiated exhaust gases were discharged through a distribution system to the plant, bacteria, and animal exposure facilities and to a manifold for chemical sampling and analysis.

EXPOSURE FACILITIES

Plant Exposures — Effluent from the irradiation chamber was piped to a lighted plant exposure chamber about 16 cubic feet in volume (Figure 8). The chamber was equipped with a system of fluorescent lamps to maintain the sensitivity of the plants. The light level was about 1000 foot-candles, high enough to keep the stomates open. Potted plants grown under greenhouse conditions were exposed. For most exposures two varieties of tobacco, pinto bean at three stages of growth, and petunia were used.

Bacteria Exposures — A rotary impactor technique was used to evaluate the effect of irradiated exhaust on bacteria (Figure 9). In this technique bacteria cultures of E. coli were plated in logarithmically increasing concentrations on a membrane filter strip, which was attached to the outer surface of a 1-1/2 inch-diameter metal cylinder. As the cylinder rotated at a constant angular velocity, a thin line of irradiated exhaust gases impinged on the surface of the membrane. After exposure, the membranes were incubated, dried, and stained, and the degree of kill was indicated by contrast between the color of the stained living colonies and the lack of color of those areas where the bacteria were killed.

Animal Exposures -- During a few runs investigations were made of the effects of short-term exposure of animals to synthetically produced smog. Rats and mice were exposed in whole-body chambers, and spontaneous running activity was evaluated. Guinea pigs were exposed through face masks; measurements included tidal volume, respiratory rate, and pulmonary flow resistance. Animals were sacrificed for various biochemical measurements. Most of the animal exposures were made during special chamber runs and are not a part of this test series.

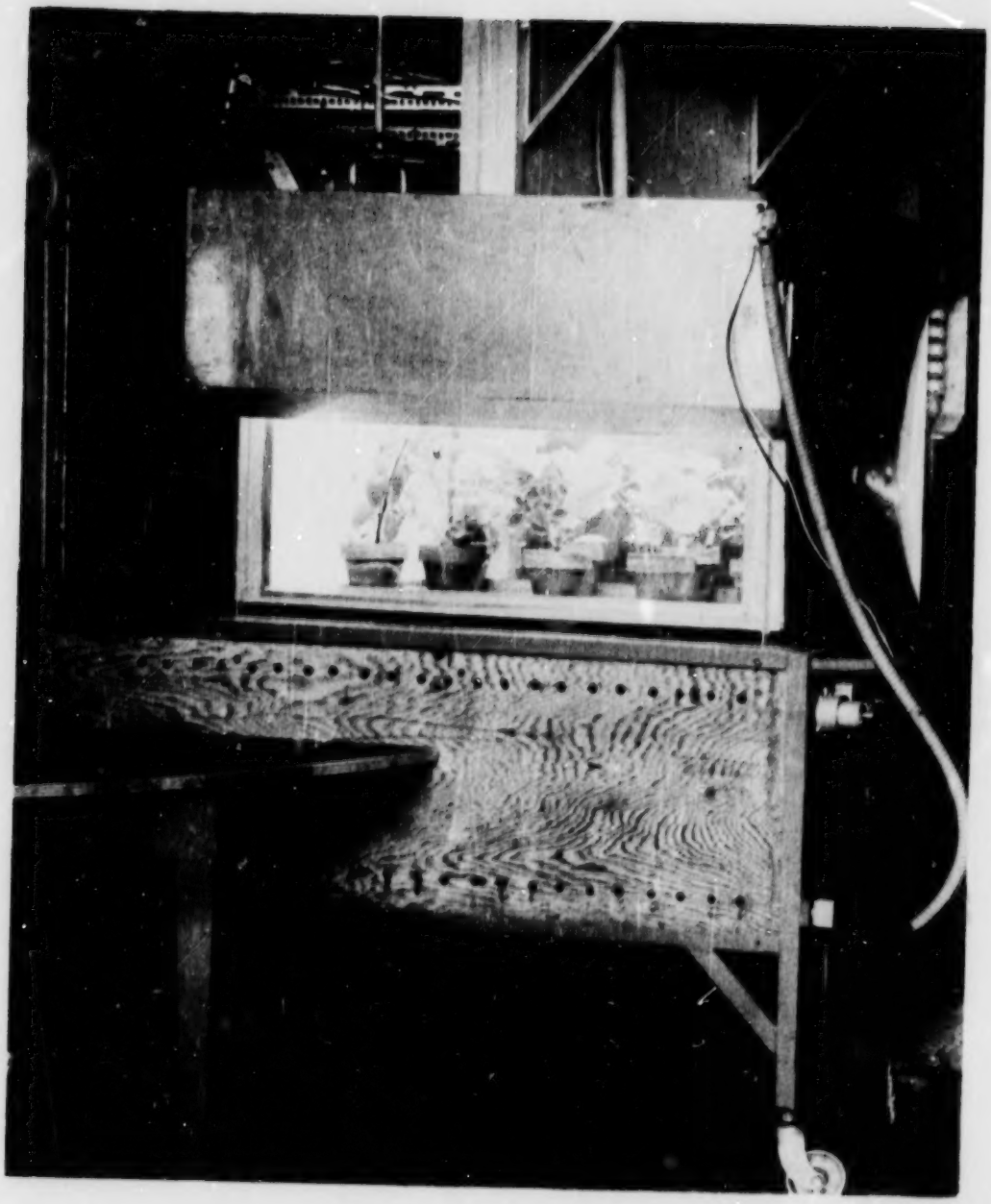

Figure 8. Plant exposure chamber.

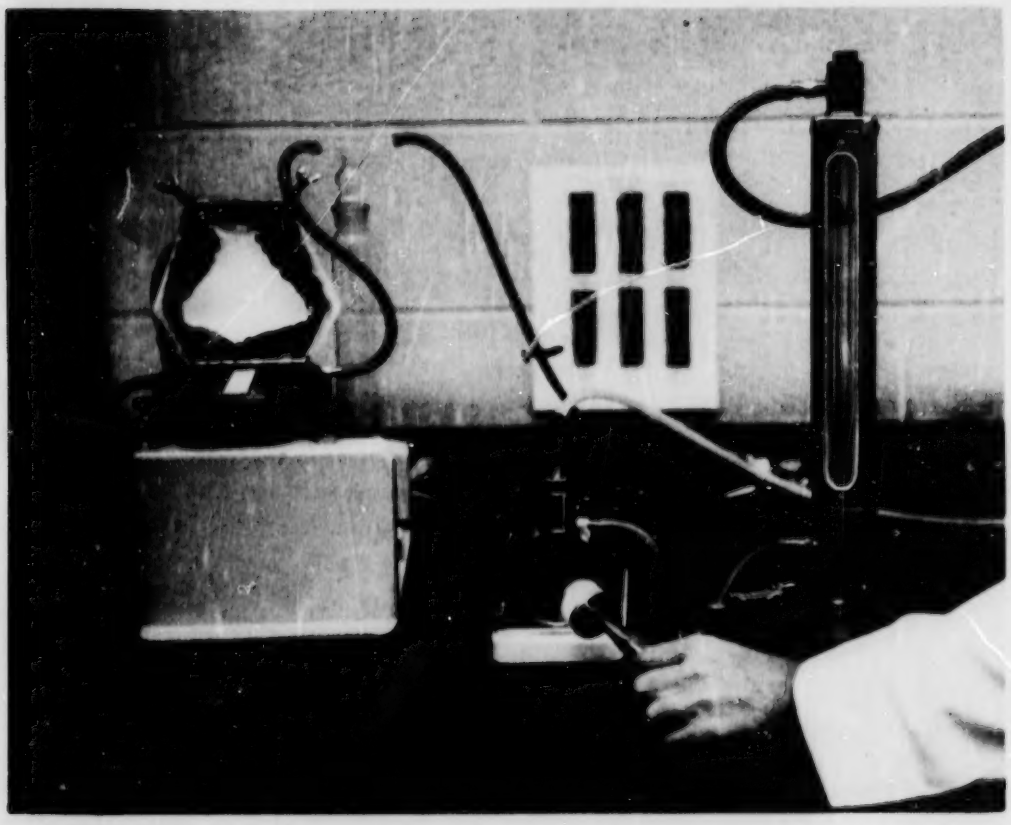

Figure 9. Bacteria exposure equipment.

ANALYTICAL PROCEDURES

Concentrations of chemical constituents were monitored in (1) the raw exhaust from the automobile, (2) the exhaust-gas mixture after dilution, and (3) the contents of the irradiation chamber before and during irradiation. Carbon monoxide, carbon dioxide, and gross hydrocarbons (as hexane) were measured in the raw exhaust gas by means of nondispersive infrared analyzers, in which a raw exhaust sample was drawn through an ice-bath condenser to remove interfering water vapor. The total hydrocarbon concentration in both the nonirradiated and irradiated exhaust gas mixture after dilution was measured with a flame-ionization-type detector, which responds in ppm total carbon atoms. NO and NO_2 were measured by a continuous-recording colorimetric instrument that uses a modified

Saltzman reagent. Because long response times are inherent in the instrument, a computer program was used to convert the instrument response to instantaneous values for NO and NO_2. Details of this procedure are given in Appendix B. Carbon monoxide concentrations in the irradiated gases were measured by means of a long-path nondispersive infrared analyzer. Oxidant concentrations were measured by a continuous-recording coulometric instrument (Mast) that uses a neutral potassium iodide solution. Gas chromatography was used for detailed analyses of hydrocarbons containing 2 to 5 carbon atoms.[4] Wet-chemical analytical methods were employed for measurement of olefin, formaldehyde, and acrolein,[5] and for confirmatory measurements for NO and NO_2.[6] A few mass-spectrographic and infrared analyses were also made.

TEST PARAMETERS

Three variables that affect the photochemical reaction system were studied in this test series.

EXHAUST CONCENTRATION

Effects of irradiation were evaluated under three conditions of concentration:

1. 'Atmospheric' hydrocarbon levels of approximately 11-15 ppm carbon. These concentrations represent ambient air levels during severe air pollution situations.
2. Concentrated hydrocarbon levels of approximately 32-40 ppm carbon.
3. 'Equivalent' atmospheric concentration levels achieved by diluting the chamber contents produced during irradiation at concentrated levels.

Variations in chemical reaction were evaluated for conditions 1 and 2. Plant exposures were made and evaluated at conditions 1 and 3. Effects on bacteria were evaluated at all three conditions.

AVERAGE IRRADIATION TIME

Average irradiation times of 85 and 120 minutes were selected to represent equilibrium conditions in the chamber after an extended period of irradiation. From the relationship previously discussed (Equation 1), average irradiation periods of 85 and 120 minutes at equilibrium (t infinite) require flow volumes of 3.9 and 2.8 cubic feet per minute respectively. At these flow volumes, for irradiation periods (i.e. time after irradiation starts) of 1.5, 2.0, and 2.5 times the average irradiation time selected, the actual average irradiation times are 78, 86, and 92 percent of the selected average irradiation time, respectively.

FUEL CONTENT

Previous work[7] indicated that the olefin content of fuels could possibly influence the air pollution potential of irradiated exhaust gases. For this reason two fuels were chosen for testing in this series, one containing 14% olefins and one containing 23% olefins. These fuels were obtained from special stocks prepared by the Western Oil and Gas Association for automotive exhaust research. Both fuels had approximately the same aromatic content: the low-olefin fuel, fuel 3, gave a bromine number of 30, and the higher-olefin fuel, fuel 5, gave a bromine number of 50. The physical specifications of the fuels were held approximately equal: both had research octane numbers of 100; ASTM distillation ranges varied by not more than 5% at any point; Reid vapor pressures were 9.3 and 9.4; and API gravities were 56.0 and 56.5. Physical and chemical properties of the fuels are shown in Table 1.

OTHER TEST CONDITIONS

Irradiation intensity in the region from 2900 to 3600 angstroms was held at levels believed to approximate summer noonday sunlight in Southern California. All tests were conducted at a constant volumetric ratio of hydrocarbon to oxides of nitrogen of approximately 12:1 (hydrocarbon expressed as ppm carbon).

The reaction system used in this test series was dynamic in that the introduction of the dilute nonirradiated exhaust gases.

Table 1. PHYSICAL AND CHEMICAL PROPERTIES OF TEST FUELS

Properties	Fuel No. 3	Fuel No. 5
API gravity, degrees	56.0	56.5
Reid vapor pressure, lb/in.^{2}	9.3	9.4
Distillation, °F		
Initial	92	95
End point	406	400
Recovery, volume %	98	97.5
Sulfur (total), weight %	0.013	0.042
Sulfur (RSH), ppm	0.0002	0.0004
Gum (existent), mg/100 ml	1.1	2.3
Gum (accelerated, 4-hr), mg/100 ml	1.4	3.2
Bromine no. (electrometric), g/100 g	31	49
Tetraethyl lead, ml/gal	0.53	1.38
Fluorescent indicator analysis (as received), volume %		
Saturates	47.1	38.8
Olefins	13.9	22.9
Aromatics	39.0	38.3
Octane no.		
Motor, F-2	88.9	87.8
Research, F-1	100.1	100.1

and the withdrawal of an equal quantity of irradiated exhaust gases was continuous. In contrast, previous studies have utilized a static system,[8, 9] in which a dilute mixture of exhaust gases was charged to the chamber, the gases were irradiated, and the effects were evaluated after a selected irradiation period. The two techniques generally produce the same series of reactions. The chief difference is that in the dynamic system the incoming nonirradiated gases and the irradiated gases present in the chamber approach kinetic chemical equilibrium, whereas in the static system the chemical reaction of the single charge is allowed to approach completion.

The extent of mixing of community atmospheres is both complex and extremely variable. On the average it is probably

greater than that which occurs in a static system and less than the continuous, uniform mixing produced in the dynamic irradiation chamber. Probably specific cases occur in which the mixing actions of both static and dynamic systems are paralleled in the atmosphere. Because of the intricate movements of parcels of air, it is possible that mixing conditions much like those produced in both systems could occur simultaneously at different locations within a community. These two test conditions represent extremes of mixing, and results obtained in both series of chamber studies probably span the average mixing conditions of the atmosphere.

CHEMISTRY OF IRRADIATED EXHAUSTS

THE NO - NO_2 REACTION PROCESS

The oxidation of NO to NO_2 is one of the significant systems in the photochemical reaction complex. Studies to date indicate that this complex reaction system consists of two fundamental reaction series: the NO - NO_2 photo-oxidation reactions and the NO_2 – free-radical reactions.

NO - NO_2 PHOTO-OXIDATION REACTIONS

Nitric oxide oxidizes to nitrogen dioxide in the presence of organic compounds under ultraviolet radiation at a rate far higher than the thermal rate of oxidation of nitric oxide by molecular oxygen. This rapid conversion of nitric oxide to nitrogen dioxide appears to require a chain reaction involving peroxyalkyl (RO_2) and peroxyacyl (RCO_3) free radicals. These radicals apparently are generated extremely rapidly by initial steps involving atomic oxygen attack on hydrocarbon species or photolysis of nitrogen dioxide.

Investigations of the photochemistry of model systems have shown that many types of organic compounds can participate in the photo-oxidation of nitric oxide to nitrogen dioxide and the formation of ozone in the photochemical reaction complex. Olefins, many aromatic hydrocarbons, some higher-molecular-weight paraffins, and aldehydes already have been shown to participate. Lower-molecular-weight paraffins (including methane, ethane, propane, and the butanes), acetylene, and benzenes do not appear to participate to any marked degree in these reactions.

NO_2 – FREE-RADICAL REACTIONS

The free-radical species that participate in the photo-oxidation of nitric oxide also may react with nitrogen dioxide to form

organic nitrogen compounds as the nitrogen dioxide concentration increases during the irradiation. Alkyl nitrates and peroxyacyl nitrates have been identified and measured as products in static chamber experiments.

Under many of the experimental conditions used in this study a substantial depletion of nitrogen dioxide was observed after the nitrogen dioxide reached its maximum concentration. A limited number of infrared measurements also indicated the presence of alkyl nitrates and peroxyacyl nitrates. The presence of these substances accounts for at least part of the decrease in the nitrogen dioxide during the irradiations.

Under dynamic irradiation conditions, photochemical reaction begins when the irradiation is started (Figure 10, Table A1).

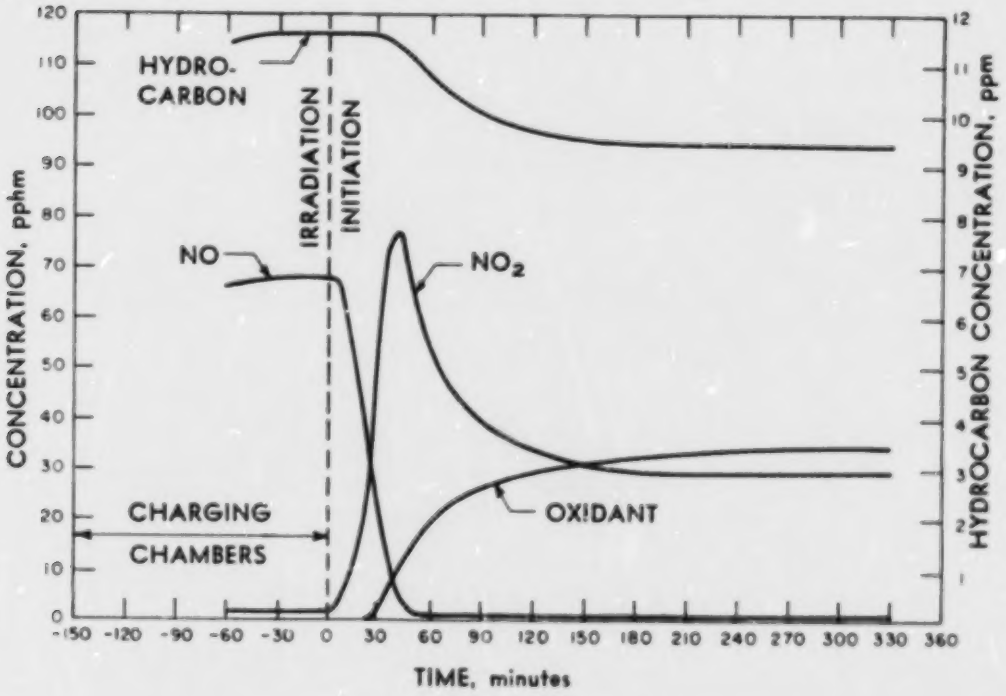

Figure 10. Chemical relationships for a typical chamber reaction.

It is postulated, as discussed above, that initially the NO-NO_2 photo-oxidation reactions predominate. This results in a rapid decrease in NO concentration, with a correspondingly rapid increase in NO_2 concentration. Some of the hydrocarbons present also decrease significantly in this stage of the reaction. This reaction continues, depending on the conditions of irradiation, for 30 to 120 minutes until the NO_2 concentration reaches a maximum and the NO concentration approaches a minimum. At about

this point the NO_2 - free-radical reactions become important, and the NO_2 concentration drops as the NO_2 reacts with intermediate exhaust reaction products. This condition continues until equilibrium is approached between the NO - NO_2 photo-oxidation reactions and the NO_2 - free-radical reaction. An increase in the level of oxidant and other reaction products and a further decrease in hydrocarbon concentration accompany the NO_2 - free-radical reactions. As similarly observed in the static irradiation systems, ozone appears only when the NO_2 reaches peak concentration and the NO approaches its minimum equilibrium concentration.

CHEMICAL EFFECTS

NO_2

The rate of formation of NO_2 is an important index for the characterization of irradiated atmospheres because it is a measure of reactivity of the over-all system, readily obtained with available monitoring instrumentation. Table 2 lists the average and individual NO_2 formation rates observed for all combinations of the test variables. These data are pictured in Figure 11. It is apparent that within the scope of the study, initial exhaust concentration had the greatest effect on NO_2 formation rate. Fuel composition had a lesser effect; average irradiation time (AIT) had little or no effect.

Table 2. NO_2 FORMATION AND DISAPPEARANCE

Test conditions			Average actual exhaust gas conc, ppm C	NO_2 Formation rate, pphm/min		Average NO_2 disappearing, %
Exhaust level	Fuel No.	AIT, min		Individual runs	Avg	
Atm	3	85	14.3	1.76, 1.25, 1.50	1.5	41.5
Atm	3	120	12.2	1.45, 1.67	1.5	60.5
Atm	5	85	14.8	1.88, 2.22	2.1	60.0
Atm	5	120	14.4	2.10, 1.95	2.0	63.0
Conc	3	85	33.0	2.42, 2.90	2.6	27.5
Conc	3	120	36.0	2.61, 2.36	2.5	35.5
Conc	5	85	39.0	3.59, 3.80	3.7	39.0
Conc	5	120	35.5	2.68, 2.74	2.7	26.5

Comparing all runs made at atmospheric hydrocarbon levels with those at concentrated levels shows a mean increase in average NO_2 formation rate from 1.8 (range 1.25-2.22) to 2.9 pphm/minute (range 2.36-3.80). Changing from a low (14%) to a high (23%) olefin fuel caused an average increase from 2.0 (range 1.25-2.9) to 2.6 pphm/minute (range 1.88-3.80). Increasing average irradiation time from 85 to 120 minutes caused a

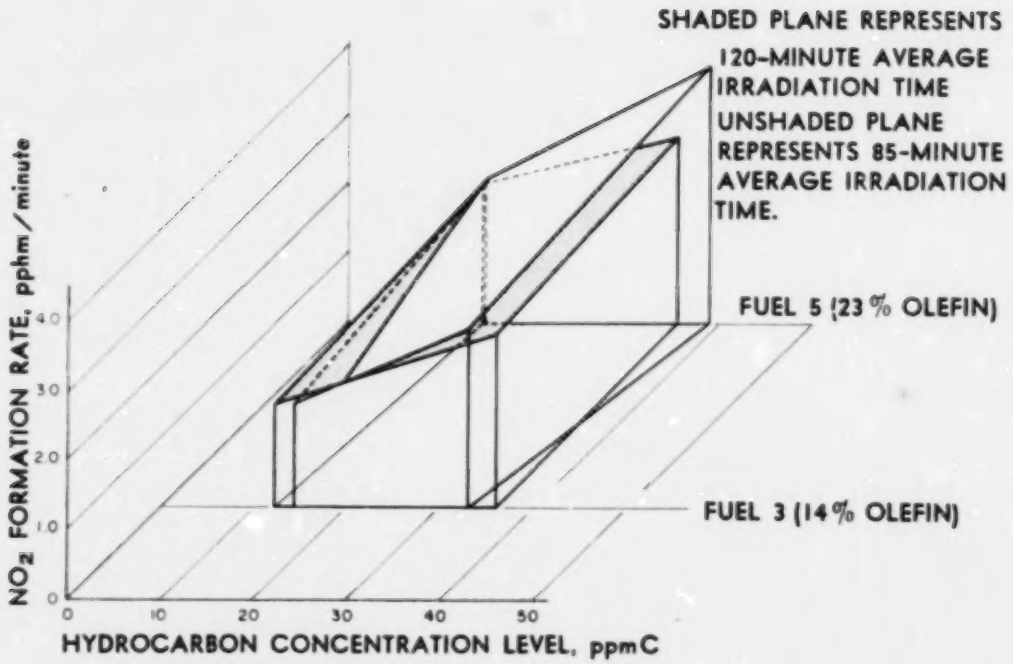

Figure 11. NO_2 formation rate as influenced by hydrocarbon concentration, fuel type, and irradiation time.

decrease from 2.5 (range 1.25-3.80) to 2.2 (range 1.45-2.74). This decrease was the result of unusual test conditions; as will be shown later essentially no change in NO_2 formation rate is attributable to changes in average irradiation time. The average differences caused by changes in concentration and fuel composition are both significant at the 1% level determined by an analysis of variance.

As shown in Figure 11, the effects of increasing initial hydrocarbon concentration and changing from fuel 3 to fuel 5 appear to be additive. This suggests that the initial olefin concentration may be the most important factor in determining the NO_2 formation rate, since both concentration and fuel influence olefin content. Table A2 gives the average concentration of four-carbon and higher olefins at the start of irradiation for each test situation. These data are plotted in Figure 12 against NO_2 formation rate and show a good relationship between olefin concentration at the start of irradiation and NO_2 formation rate.

Consideration of the importance of olefin concentration in the initial exhaust mixture also helps explain the apparent decrease in NO_2 formation rate as the average irradiation time (AIT) increased from 85 to 120 minutes in the concentrated series with fuel 5 (Figure 11). Although the total hydrocarbon concentrations were similar, the exhaust mixture for the runs at 85 minutes AIT contained an average of 6.57 μg/l of C_4^+ olefins and that used in the runs at 120 AIT averaged 3.82 μg/l.

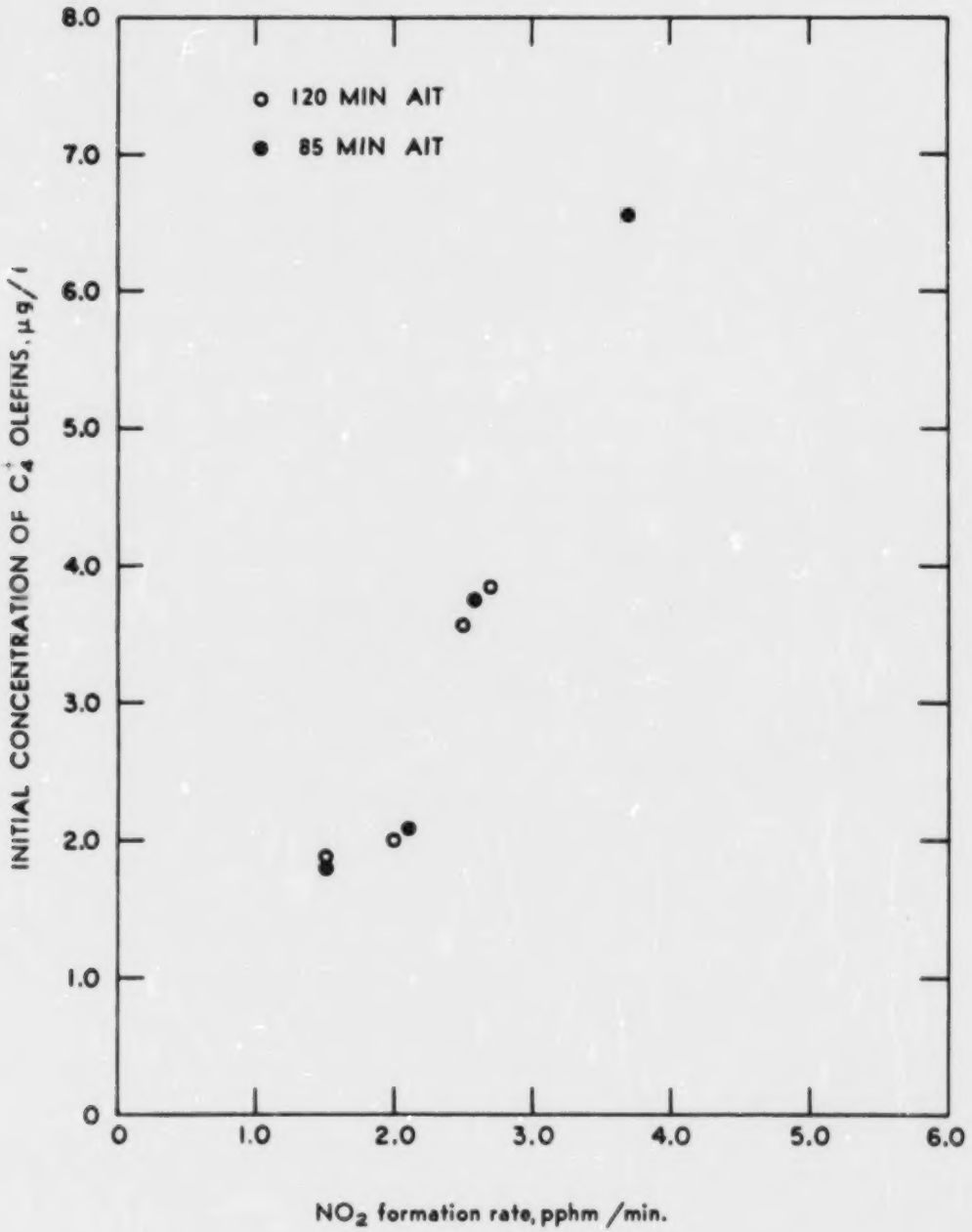

Figure 12. Relationship of olefin concentration to NO_2 formation rate.

The apparent difference in NO_2 formation rate (3.1 vs 2.7 pphm/min) is probably not due to changes in AIT but to initial olefin concentration. Adjustment of these points to similar olefin concentrations brings them into line and leads to the conclusion that AIT has no influence on NO_2 formation rate. The experimental conditions that led to the low olefin levels for the 120-minute AIT cannot be explained.

Analysis of the NO_2 - free-radical reaction data does not allow conclusions as detailed as for the NO_2 formation rate. The rate of NO_2 disappearance cannot be established accurately, since limitations in the instrumentation prevented the precise determination of the time of peak NO_2 concentration. Therefore the percentage of NO_2 disappearing (defined as the percent decrease in NO_2 concentration from peak to equilibrium) has been used as a measure of the NO_2 - free-radical series of reactions described earlier. Analysis of the data in Table 2 indicates that NO_2 disappearance is greater for the atmospheric series of tests than for the concentrated series. Average values drop from 56% disappearance for the atmospheric series to 32% for the concentrated series. This difference is significant at the 1% level. The differences caused by fuel composition (41 and 47%) and average irradiation time (42 and 46%) are not statistically significant.

OXIDANT

One of the principal reactions associated with the NO to NO_2 photo-oxidation is the formation of oxidant (Figure 10). The coulometric instrument used to monitor ozone is sensitive to NO_2 and other oxidants as well as to ozone. To secure a better indication of ozone levels, corrections were made for the principal interference, NO_2. The corrected values for oxidant, shown in Figure 13, are primarily ozone, although they include, to a very limited degree, the response of other oxidants.

Two conclusions are apparent from the oxidant data: (1) average irradiation time has no influence on oxidant production and (2) the higher initial hydrocarbon concentration level inhibits the production of oxidant for as much as 1/2 hour at the beginning of the irradiation. Although variations in oxidant level were observed with changes in exhaust concentration and fuel composition, these followed no consistent pattern and provide no basis for general conclusions. By contrast, reports of static irradiation chamber tests[8] indicate that ozone formation increased with exhaust concentration as a function of the one-half power of the increase in hydrocarbon level. Additional work is needed to resolve the apparent difference between the results of static and dynamic tests.

HYDROCARBONS

The disappearance of hydrocarbons during irradiation is in accord with the NO_2 - free-radical reactions hypothesis, i.e. the involvement of NO_2 with intermediate hydrocarbon reaction products. The disappearance of hydrocarbons also could be the result of reactions involving ozone and oxygen atoms to form oxygenated products. In all tests the reduction in organics as

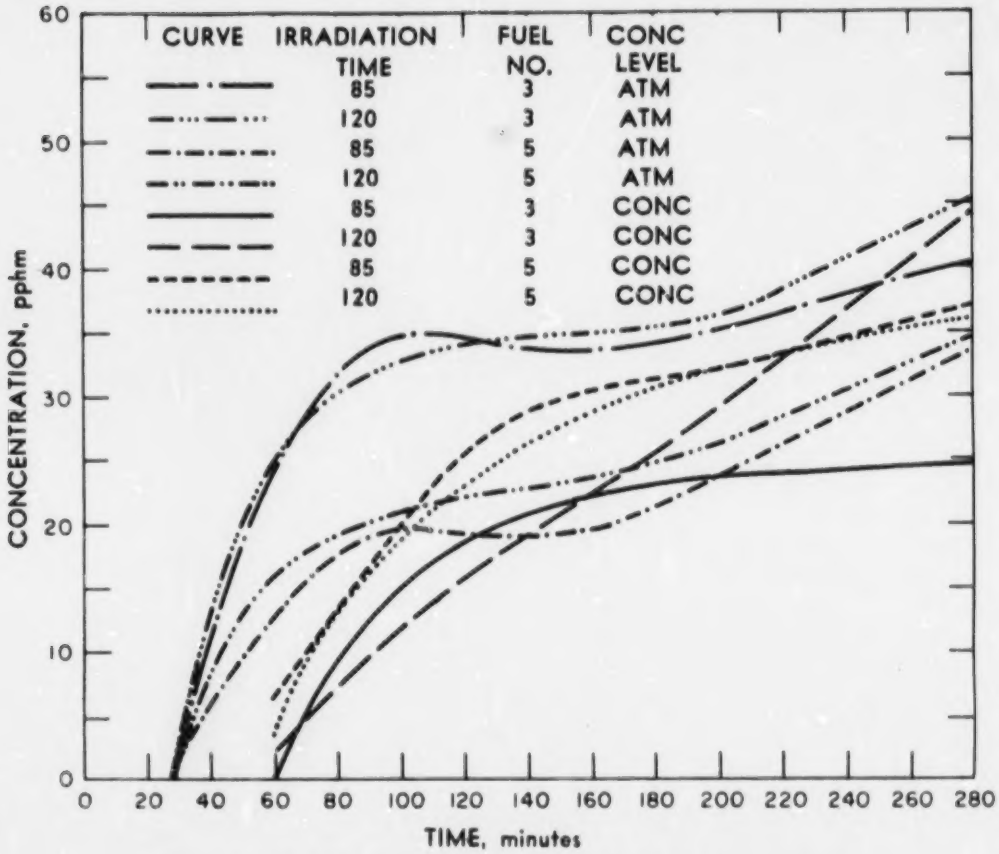

Figure 13. Oxidant concentrations corrected for NO_2 response.

measured by the flame-ionization analyzer was not appreciable until the NO_2 concentration peaked (Appendix A, Figures A1 through A8). At this point the reduction increased sharply and continued until chamber equilibrium was reached. The over-all reduction ranged from 15 to 20% for all test conditions.

A consistent difference was noted in the reactivity of the various classes of hydrocarbons as measured by the percent decrease in concentration of these individual species. These reactivities were not influenced by changes in exhaust concentration, fuel composition, or irradiation time, however.

Olefins were studied by both wet chemistry and gas chromatography. Four-carbon and higher molecular weight olefins were measured by a wet chemical procedure, the p-dimethylaminobenzaldehyde method of Altshuller and Sleva.[10] Aromatics and two- through five-carbon paraffins and olefins, acetylene and methyl acetylene were analyzed by gas chromatography.[4, 11]

Measurements made for acetylene indicated no significant reaction rate for this compound, but methyl acetylene appeared to be slightly reactive. Tables A2 - A5 give data on concentra-

tion of four- and five-carbon paraffins for the various test conditions. Table 3 summarizes losses of these paraffins during irradiation. It appears that on the average four- and five-carbon paraffins did not react at significant rates.

Table 3. PERCENT DECREASE FOR SPECIFIC HYDROCARBONS

Compound	Fuel No. 3			Fuel No. 5			
	85 Min		120 Min[b]	85 Min		120 Min	
	Atm	Conc	Atm	Atm	Conc	Atm	Conc
Di olefin							
Butadiene	68	62	73	67	67	75	65
Terminally bonded olefins							
Butene-1, isobutene	62	60	75	52	71	67	68
Pentene-1	47	55	67	36	57	63	60
2-Methylbutene	71	67	77	75	88	88	68
Avg	62	61	73	58	71	73	65
Internally bonded olefins							
c-Butene-2	100[a]	100[a]	100[a]	100[a]	100[a]	100[a]	100[a]
t-Butene-2	100[a]	100[a]	100[a]	100[a]	100[a]	100[a]	100[a]
c-Pentene-2	90	86	100[a]	100[a]	96	100[a]	100[a]
t-Pentene-2	90	81	100[a]	100[a]	95	100[a]	100[a]
2-Methylbutene-2	98	87	100[a]	100[a]	93	100[a]	100[a]
Avg	96	85	100[a]	100[a]	95	100[a]	100[a]
Paraffins							
Isobutane	10	4	13	-4	4	0	-5
n-Butane	14	5	3	3	-13	2	-2
Isopentene	13	6	10	-3	-5	5	0
n-Pentene	12	8	10	-3	-3	5	6
Avg	12	6	9	-2	-4	3	0

[a]Values after irradiation are below the limits of detection; although percent decrease is approximate, it usually approaches 100 percent.
[b]No values are given for concentrated levels, since data were inadequate for analysis.

Olefins – Although all olefins measured showed a significant decrease in concentration during the test runs, the decrease was not influenced by the test variables. The relative concentration of the individual olefins at the start of irradiation was dependent on fuel composition and did vary to some extent with initial exhaust concentration. These data are shown in Tables A2 - A5.

Individual four- and five-carbon olefins reacted at rates that were dependent upon the location of the double bond (Table 3). The terminal olefins showed an average decrease of approximately 65% after irradiation periods of 170 minutes for the 85-minute AIT series and 240 minutes for the 120-minute AIT series. At the end of these same irradiation periods, all internally bonded olefins showed almost complete reaction. The final concentrations for internally bonded olefins were usually below the limits of detection of the analytical methods. Butadiene-1, 3 behaved similarly to the terminally bonded olefins. Decreases of 12% and 50% were found for ethylene and propylene, respectively, in a few gas-chromatographic measurements

of these compounds in the atmospheric series. Static irradiation chamber tests[9, 12] also show a high degree of reactivity for terminally bonded olefins and essentially complete disappearance of internally bonded olefins.

Aromatics – Aromatics were studied in a few runs by gas chromatography.[11] The chromatographic column used did not provide resolution for complete separation of benzene from other reaction products. Work with the mass spectrometer,[13] confirmed by pure component studies, indicated that benzene is nonreactive. All other aromatics studied showed some degree of reactivity after an irradiation period equal to two times the average irradiation time. The results of three runs, all made with fuel 3 in the concentrated series, are shown in Table 4. These few tests indicated an average decrease of about 10% for toluene and ethylbenzene, about 30% for xylene and the 3- and 4-ethyltoluenes, and about 50% for styrene.

Table 4. PERCENTAGE CHANGE IN AROMATIC HYDROCARBONS[a]

AIT[b]	Toluene	Ethyl-Benzene	m- and p-Xylene	o-Xylene	Styrene	3- and 4-Ethyltoluene
120	- 5	0	-21	-29	-40	-21
120	-13	-17	-28	-29	-70	-39
85	- 6	-16	-27	-27	[c]	[c]
Avg	- 8	-11	-25	-28	-55	-30

[a]Percent change after irradiation periods of 170 and 240 minutes for 85 and 120 minute AIT, respectively.
[b]Average irradiation time, minutes.
[c]Concentrations of these components too low to determine changes in composition.

These results indicate that the nature of substitution on the benzene ring controls the reactivity rate. More detailed evaluation of this possibility is not warranted by the limited experimental data available.

FORMALDEHYDE

Formation of formaldehyde in the irradiation system depended primarily on initial exhaust concentration, as shown in Figure 14. Increasing initial exhaust concentration by 2 to 2-1/2 times generally resulted in a proportional increase in formaldehyde after 240 minutes of irradiation, although the initial formation rates appear about the same for each exhaust concentration. These average data also indicate that fuel composition may influence slightly the production of formaldehyde. Average irradiation time did not appear to influence formaldehyde production.

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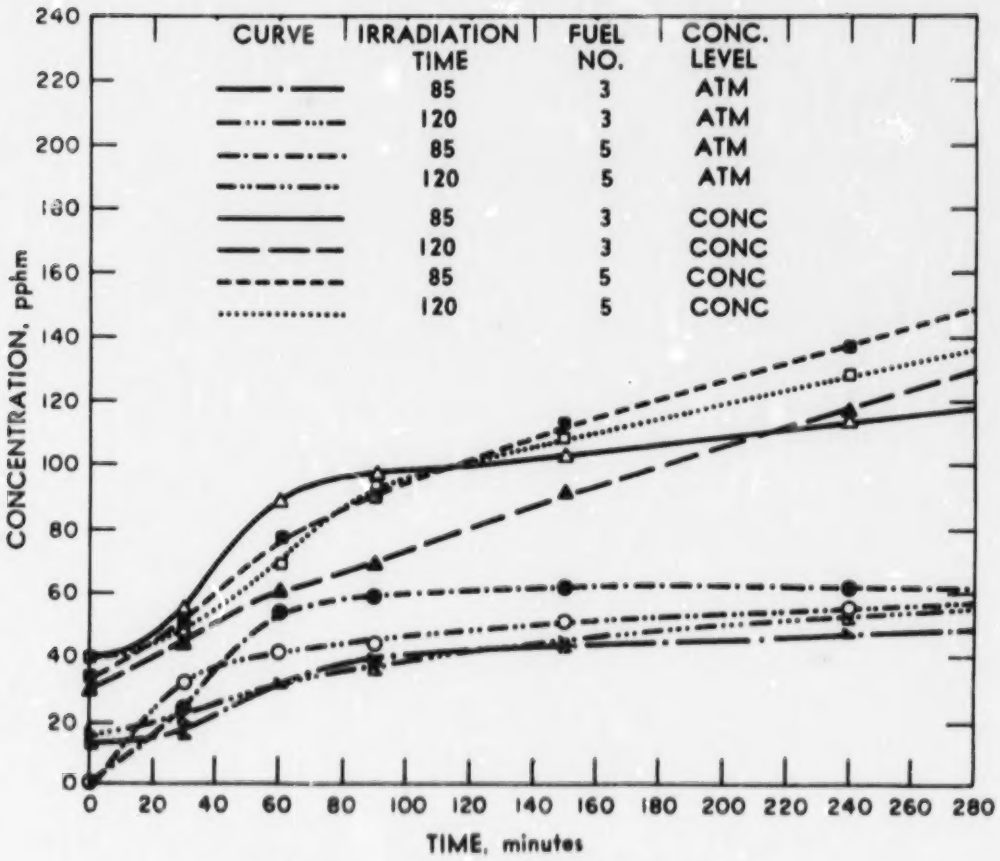

Figure 14. Formaldehyde concentrations.

OTHER ALDEHYDES

Aldehydes other than formaldehyde were measured in a few runs and were found both in the nonirradiated and the irradiated exhaust mixtures. Irradiation brought about a five-fold increase in their concentration; that is, only about 20% of the aldehyde came directly from the auto exhaust. Acrolein, analyzed by the method of Cohen and Altshuller,[5] behaved generally like formaldehyde; the concentration was initially low, increased during irradiation, and reached a maximum after approximately two average irradiation times. In several analyses a 25 to 30% decrease in acrolein concentrations, noted after the maximum was reached, indicated further reaction of the acrolein.

Aldehydes showed the same general relationships to initial exhaust concentration and fuel composition as the NO_2 formation rate – indicating a dependency on initial olefin concentration. This is not unexpected, since it is the attack of ozone and atomic oxygen on the olefins and aromatics that produces aldehydes. In this study, however, the aromatic content of the fuels was held

constant. Increasing the concentration level of exhaust in the chamber and changing from fuel 3 to fuel 5 both resulted in an increase in the aldehydes produced. The reaction that produces acrolein, primarily from the butadiene-1, 3 is typical of the aldehyde-producing reactions:

$$CH_2 = CH\text{-}CH{=}CH_2 + (0) \longrightarrow CH_2{=}\ CH\text{-}CHO + CH_2O + \text{other products.}$$

In two instances total aldehydes were also determined by the 3-methyl-2-benzothiazolone hydrazone test described by Sawicki et al.[14] Table 5 shows the relationship between formaldehyde[15] and total aldehydes for the tests with fuel 3 at concentrated exhaust levels and 85-minute AIT. Approximately 60% of the total aldehydes were formaldehyde in these runs.

Table 5. ALIPHATIC ALDEHYDE CONCENTRATION[a] (ppm)

Run	Total aldehydes[b]	Formaldehyde[c]	% Formaldehyde
1	2.25	1.11	49
	1.90	1.28	67
2	1.61	0.96	60
	1.95	1.02	52
		Average	57

[a]Concentration after equilibrium is attained.
[b]Total aldehydes corrected for formaldehyde; absorptivity of 40 is used for all aldehydes other than formaldehyde.
[c]As determined by the chromotropic acid method.[12]

BIOLOGICAL EFFECTS

PLANTS

Plants were exposed to two types of irradiated gases: (1) directly to chamber gases irradiated at the atmospheric exhaust levels, and (2) to chamber gases irradiated at the high exhaust concentration, but diluted to atmospheric levels before plant exposure. Exposures started within 15 minutes after the chamber lights were turned on, and usually continued for 4 hours. Following exposure, plants were returned to the greenhouse and held for observation over a period of time.

Symptoms of severe injury were sometimes noticeable within a few hours. Some injury patterns were not visible until 48 hours after exposure. The patterns of injury, including the microscopic patterns observed with thin sections, varied with species and age of tissue. Prior- and post-exposure culture conditions had some effect on injury pattern.

Broad classes of injury patterns are thought to relate to specific phytotoxicant classes. At this time, however, techniques of exposure and classification of injury patterns have not been developed sufficiently for formulation of a multiple-class injury scale.

A number of general conclusions are possible concerning the effect of the three variables on plant damage: (1) fuel 5 produced a greater total injury than fuel 3 and also a different distribution of type of injury, and (2) higher exhaust concentrations at time of irradiation also produced a different distribution of type of injury than the atmospheric series, but tended to decrease the total injury. (It should be noted that the higher exhaust concentrations were diluted to atmospheric levels after irradiation and before plant exposure.) For reporting gross injury a scale of 0 (no injury) to 4 (total injury of sensitive tissue) was used. The average index for all plants is shown in Table 6 for each fuel at each irradiation time and concentration.

Table 6. AVERAGE GROSS PLANT INJURY[a]

Fuel	Irradiation time, min	Irradiation concentration, ppm C	Plant injury[b]
3	85	12-15	1.0
		32-40[c]	0.4
	120	12-15	0.5
		32-40[c]	0.2
5	85	12-15	2.1
		32-40[c]	1.8
	120	12-15	2.2
		32-40[c]	1.0

[a]Average of all plants exposed at each condition.
[b]Scale: 0 (no injury) to 4 (total injury of sensitive tissue).
[c]Plants exposed after dilution of exhaust to equivalent atmospheric carbon levels.

ANIMALS

Although animal exposures were made during only a few of the irradiation chamber runs discussed in this report, the facilities were used in special tests designed specifically for animal studies. The conditions of these tests did not necessarily conform to those used for the chemical, plant, and bacteria studies discussed in this report and are not a part of this test series. These special investigations with small animals, which were generally exploratory studies, are summarized in detail in a report prepared by the Laboratory of Medical and Biological Sciences, Division of Air Pollution.[16]

BACTERIA

The effects of the irradiated gases on bacteria (E. coli) are shown in Table 7.

Table 7. EFFECT OF CONCENTRATION ON BACTERIA KILL

Fuel No.	Irradiation time, min	Irradiation level	Bacteria kill, relative units[a]	
			Exposure at irrad. level[b]	Exposure at atm level[c]
3	85	Atm	2.0	2.0
		Conc	9.0	1.5[b]
	120	Atm	4.0	4.0
		Conc	6.5	1.0[b]
5	85	Atm	1.5	1.5
		Conc	9.0	2.0[b]
	120	Atm	2.5	2.5
		Conc	8.0	2.0[b]

[a]Complete kill equals 9; exponential scale.
[b]Exposure made at the concentration at which irradiation occurred.
[c]Exposure made after dilution of the high-concentration exhaust to equivalent atmospheric concentration levels.

The values for bacteria kill shown in Table 7 represent degree of bacteria kill (rated on a scale of 1 through 9). They were determined by visually estimating the area and distribution of prepared culture strip affected by exposure to the irradiated exhaust. Since the bacteria were plated on the test strip in concentrations that increased logarithmically, the degree of kill given in Table 7 represents an exponential rather than a linear kill scale.

Degree of bacteria kill was influenced only by exhaust concentration. No effect was observed for changes in fuel composition or average irradiation time. No difference in bacteria kill was noted between exposure to gases irradiated at atmospheric

levels and gases irradiated at concentrated levels and diluted to atmospheric levels.

SUMMARY OF RESULTS

Within the limits of experimental values selected for this series of tests, the three major variables examined, (1) initial exhaust composition, (2) fuel composition and (3) average irradiation time can be ranked according to their influence on the chemistry of the irradiation process, and biological effects of reaction products. Concentration of exhaust at the start of irradiation produced the greatest effect on the greatest number of test parameters, including NO_2 formation rate, oxidant and formaldehyde production, plant damage, and bacterial kill. Changing fuel from number 3 (14% olefins) to number 5 (23% olefins) also affected plant damage, NO_2 formation rate, and possibly formaldehyde production. Changing average irradiation time from 85 to 120 minutes had essentially no effect on any of the test parameters.

More detailed conclusions are appropriate for each of the test parameters and are given below:

1. The NO_2 formation rate was increased significantly by increases in both exhaust concentration and olefin content of the fuel. Average NO_2 formation rate increased from 1.8 to 2.9 pphm/min as the average initial exhaust concentration increased from atmospheric levels (14 ppm C) to concentrated levels (36 ppm C). An average increase from 2.0 to 2.6 pphm/min was observed in going from fuel number 3 to fuel number 5. Increasing average irradiation time from 85 to 120 minutes had no effect on NO_2 formation rate. A good relationship was observed between NO_2 formation rate and initial olefin concentration in the chamber.

2. The percentage of disappearance of NO_2 was decreased significantly by increasing initial exhaust concentration. Fuel composition and average irradiation time had no effect.

3. Increasing exhaust concentration appeared to cause a delay in initial oxidant production of approximately 30 minutes. The amount of oxidant (mostly ozone) produced was influenced by exhaust concentration and fuel type, but no consistent pattern was apparent. Average irradiation time had no apparent effect on oxidant production.

4. Reduction in organic concentration as measured by the flame-ionization analyzer ranged from approximately 15 to 25%. The percentage decrease in the terminal olefin varied between 35% and 88%, depending on the specific hydrocarbon, and averaged about 65% decrease in concentration with irradiation. All internally bonded olefins reacted almost completely to form products. Paraffins and acetylene were essentially unreactive. The aromatic hydrocarbons disappeared through reaction by amounts ranging from about 10% for toluene to about 50% for styrene and appeared to depend on type of substitution on the benzene ring. No consistent patterns of influence of exhaust concentration, fuel type, or average irradiation time were observed for any group of hydrocarbons.

5. Increasing initial exhaust concentration from 14 ppm carbon to 36 ppm carbon resulted in proportional increases in average formaldehyde concentrations of from 50 pphm to 120 pphm at kinetic equilibrium.

6. In a few test runs analyses were made for both total aldehydes and formaldehydes. Approximately 60% of the total aldehydes appeared to be formaldehydes.

7. Most of the aldehyde present came from chamber reactions. (About 20% originated in the auto exhaust.) Generally aldehydes varied with exhaust concentration and fuel type similarly to the NO_2 formation rate — indicating a dependency on initial olefin concentration. This was as expected, since the attack of ozone and atomic oxygen on olefins produces most of the aldehyde present.

8. Differences in extent and distribution of type of plant damage were observed with changes in exhaust concentration at irradiation and with fuel type. No effects were attributable to changes in average irradiation time. The high-olefin fuel generally gave a higher injury index than did the low-olefin fuel. Plants exposed to exhaust irradiated at 36 ppm carbon and diluted to the 14-ppm equivalent prior to plant exposure generally gave a lower injury index than plants exposed to exhaust irradiated at 14 ppm carbon.

9. The average degree of bacterial kill increased from 3 to 8 on an exponential scale as irradiated exhaust concentration increased from 14 to 36 ppm carbon. When the concentrated irradiated mixture was diluted to atmospheric levels, the degree of kill decreased to a value of about 2. Fuel composition and average irradiation time had no apparent effect on degree of bacterial kill.

In addition to the results enumerated above, this first series of dynamic irradiation chamber investigations has demonstrated the usefulness and versatility of the facility, permitted development of reliable experimental and analytical techniques, suggested possibilities for future investigations, and provided the basis for their design. A second series of tests with the dynamic irradiation chamber has been completed, and analysis of data is now under way. These runs were designed to explore in detail the effects of varying ratios of hydrocarbon to oxides of nitrogen. Tests were run with a single fuel (similar to fuel 3), 120-minute average irradiation time, and exhaust concentrations at atmospheric levels or below. A report is being prepared on this second series. Additional test series will follow.

Investigations of the effect of raw and irradiated exhaust on animals have been greatly expanded and transferred to a separate facility since this first series of tests. The present study involves nearly 3000 small animals and continuous exposures over the life period of the animals to varying levels of raw and irradiated exhaust.

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APPENDIX A

RAW DATA FOR IRRADIATION CHAMBER REACTION PRODUCTS

Table A1. CONCENTRATION VERSUS TIME AFTER IRRADIATION STARTED
(Mean values from two or more tests)

Product	Fuel No.	Average ir.ad. time, min	Atmospheric levels (11-15 ppm carbon) 0 Min	30 Min	60 Min	90 Min	150 Min	240 Min	Concentrated levels (32-40 ppm carbon) 0 Min	30 Min	60 Min	90 Min	150 Min	240 Min
NO (pphm)	3	85	62.3	27.3	1.7	1.7	1.3	1.0	214.5	150.0	50.8	22.3	16.9	16.9
	3	120	79.0	21.5	0.5	0.5	0.5	0.5	195.8	159.2	73.3	38.9	25.2	20.6
	5	85	62.0	6.5	1.5	2.0	2.0	2.0	216.1	137.1	17.3	16.1	16.1	14.8
	5	120	35.0	4.0	0.5	0.0	0.0	0.0	159.4	102.7	30.6	20.3	18.8	17.1
NO_2 (pphm)	3	85	2.3	61.5	52.3	44.5	43.0	42.3	14.9	83.1	176.1	173.6	151.3	148.8
	3	120	3.0	62.0	50.5	38.0	31.0	27.0	14.9	69.8	161.4	210.7	203.8	134.6
	5	85	2.5	74.0	36.5	31.5	31.0	28.5	19.7	114.9	182.8	158.1	135.8	129.7
	5	120	2.0	62.5	36.0	31.0	29.0	29.0	18.2	101.6	200.1	179.3	156.2	145.1
HC (ppm)	3	85	14.3	14.3	13.2[a]	12.3	12.0	12.0	33.0	33.0	31.5[a]	29.5	27.8	28.0
	3	120	12.2	12.1	11.1	10.6	10.2[a]	10.4	36.0	36.0	33.8	32.9	31.1	30.8
	5	85	14.8	14.3	12.4	11.8[a]	11.5	10.9	39.0	39.0	36.0	34.5	33.0	33.0
	5	120	14.4	13.5	12.1	11.5[a]	11.1	11.3	35.5	35.5	33.0	30.5	29.5	29.0
Oxidant (pphm)	3	85	0.0	0.5	24.1	33.5	33.1	36.5	0.0	0.0	0.0	2.0	21.3	23.4
	3	120	0.0	2.0	25.0	31.5	33.5	37.5	0.0	0.0	2.0	9.0	20.2	32.5
	5	85	0.0	2.0	12.5	19.0	19.0	26.0	0.0	0.0	6.5	16.0	29.8	32.8
	5	120	0.0	2.0	15.8	19.5	23.3	28.0	0.0	0.0	3.5	16.3	27.5	32.8
Olefin (pphm)	3	85	16.1	12.9[a]	5.6	3.3	2.8[a]	2.7	45.5	41.2[a]	25.5	20.6[a]	16.4[a]	15.0
	3	120	21.4	17.1[a]	9.2	6.0[a]	3.6	2.8[a]	47.0	44.0[a]	32.0	18.1[a]	11.2[a]	8.0
	5	85	46.0	35.0[a]	14.9[a]	10.8[a]	7.3[a]	6.2	69.4	61.0[a]	25.5	20.2[a]	15.0[a]	12.2
	5	120	35.6	28.0[a]	12.8[a]	8.7[a]	5.0[a]	3.9	54.4	52.3[a]	37.4	20.5[a]	13.3[a]	9.0
HCHO (pphm)	3	85	13.7	15.3[a]	31.0[a]	39.7	43.3[a]	46.7	39.5	54.0	89.0[a]	97.0[a]	103.0	113.5
	3	120	15.0	21.5	31.5[a]	36.5[a]	44.5[a]	53.0	29.0	44.0	60.5	68.5	92.55	116.5
	5	85	0.0	23.0	54.0[a]	58.5	61.5[a]	61.5	33.5	50.0	77.0	90.0[a]	112.5	137.0
	5	120	0.0	32.0	40.5[a]	43.0	46.5	54.0[a]	40.0	46.5	68.5	93.0	107.5	128.0

[a]Interpolated value.

Table A2. HYDROCARBON REACTIONS; CONCENTRATED SERIES - FUEL No. 3

Compound	85-Min avg irradiation time			120-Min avg irradiation time		
	Concentration, ppm[a]			Concentration, ppm[a]		
	Before[b]	After[c]	% Decrease	Before[b]	After[c]	% Decrease
Diolefin						
Butadiene	0.047	0.018	62	0.026	0.021	19
Terminally bonded olefins						
Butene-1, isobutene	0.094	0.038	60	0.052	0.045	13
Pentene-1	0.031	0.014	55	0.014	0.015	0
2-Methylbutene-1	0.049	0.016	67	0.031	0.017	45
Average			61			
Internally bonded olefins						
c-Butene-2	0.013	0.005>N[e]	> 62	0.006	0.005>N[e]	> 13
t-Butene-2	0.015	0.005>N	> 67	0.008	0.005>N	> 37
c-Pentene-2	0.049	~ 0.007	~ 86	0.021	0.005>N	> 76
t-Pentene-2	0.086	0.016	81	0.042	0.005>N	> 88
2-Methylbutene-2	0.101	0.013	87	0.068	0.009	87
Average			85			~ 90[f]
C_4 + olefins[d]	3.78	1.50	60	3.64	0.8	78
Paraffins						
Isobutane	0.027	0.026	4	0.008	0.022	
n-Butane	0.222	0.212	5	0.087	0.188	
Isopentane	0.313	0.294	6		0.289	
n-Pentane	0.107	0.098	8		0.106	
Average			6			

[a]Average values for two or more runs.
[b]Chamber concentration before irradiation.
[c]Chamber concentration after two average residence times.
[d]Olefins determined by wet chemical analysis (6); results in micrograms per liter.
[e]Values are less than stated value, which is limit of detection.
[f]Average value is estimated; actual value is not determinable because of limit of detection.

Table A3. HYDROCARBON REACTIONS, CONCENTRATED SERIES - FUEL No. 5

Compound	85-Min avg irradiation time			120-Min avg irradiation time		
	Concentration, ppm[a]			Concentration, ppm[a]		
	Before[b]	After[c]	% Decrease	Before[b]	After[c]	% Decrease
Diolefin						
Butadiene	0.072	0.024	67	0.046	0.016	65
Terminally bonded olefins						
Butene-1, isobutene	0.105	0.030	71	0.088	0.028	68
Pentene-1	0.044	0.019	57	0.045	0.018	60
2-Methylbutene-1	0.110	0.013	88	0.076	0.024	68
Average			71			65
Internally bonded olefins						
c-Butene-2	0.029	0.005>N[e]	>83	0.024	0.005>N[e]	>79
t-Butene-2	0.030	0.005>N	>84	0.024	0.005>N	>79
c-Pentene-2	0.068	~0.003	~96	0.054	0.005>N	>91
t-Pentene-2	0.127	~0.006	~95	0.101	0.005>N	>95
2-Methylbutene-2	0.145	0.010	93	0.093	0.005>N	>95
Average			95			~85[f]
C_4 + Olefin[d]	6.57 µg	2.37	64	3.82	0.68	82
Paraffins						
Isobutane	0.028	0.027	4	0.022	0.023	-5
n-Butane	0.189	0.213	-13	0.165	0.169	-2
Isopentane	0.409	0.428	-5	0.316	0.317	0
n-Pentane	0.120	0.123	-3	0.098	0.092	6
Average			-4			0

[a]Average values for two or more runs.
[b]Chamber concentration before irradiation.
[c]Chamber concentration after two average residence times.
[d]Olefins determined by wet chemical analysis (6); results in micrograms per liter.
[e]Values are less than stated value, which is limit of detection.
[f]Average value is estimated; actual value is not determinable because of limit of detection.

Table A4. HYDROCARBON REACTIONS; ATMOSPHERIC SERIES - FUEL No. 5

Compound	85-Min avg irradiation time			120-Min avg irradiation time		
	Concentration, ppm[a]			Concentration, ppm[a]		
	Before[b]	After[c]	% Decrease	Before[b]	After[c]	% Decrease
Diolefin						
Butadiene	0.030	0.010	67	0.024	0.006	75
Terminally bonded olefins						
Butene-1, isobutene	0.040	0.019	52	0.036	0.012	67
Pentene-1	0.022	0.014	36	0.019	0.007	63
2-Methylbutene-1	0.073	0.018	75	0.052	0.006	88
Average			58			73
Internally bonded olefins						
c-Butene-2	0.016	0.001>N[e]	>94	0.014	0.001>N	>93
t-Butene-2	0.016	0.001>N	>94	0.014	0.001>N	>93
c-Pentene-2	0.045	0.001>N	>98	0.035	0.001>N	>97
t-Pentene-2	0.085	0.001>N	>99	0.068	0.001>N	>99
2-Methylbutene-2	0.151	0.001>N	>99.4	0.129	0.001>N	>99
Average			~99[f]			~99[f]
C_4 + Olefin[d]	2.07 µg	0.40	81	2.0 µg	0.26	87
Paraffins						
Isobutane	0.023	0.024	-4	0.015	0.015	0
n-Butane	0.154	0.150	3	0.110	0.108	2
Isopentane	0.232	0.240	-3	0.194	0.184	5
n-Pentane	0.072	0.074	-3	0.058	0.055	5
Average			-2			3

[a]Average values for two or more runs.
[b]Chamber concentration before irradiation.
[c]Chamber concentration after two average residence times.
[d]Olefins determined by wet chemical analysis (6); results in micrograms per liter.
[e]Values are less than stated value, which is limit of detection.
[f]Average value is estimated; actual value is not determinable because of limit of detection.

Table A5. HYDROCARBON REACTIONS; ATMOSPHERIC SERIES - FUEL No. 3

Compound	85-Min avg irradiation time			120-Min avg irradiation time		
	Concentration, ppm[a]			Concentration, ppm[a]		
	Before[b]	After[c]	% Decrease	Before[b]	After[c]	% Decrease
Diolefin						
Butadiene	0.025	0.008	68	0.022	0.006	73
Terminally bonded olefins						
Butene-1, isobutylene	0.042	0.016	62	0.040	0.010	75
Pentene-1	0.017	0.009	47	0.012	0.004	67
2-Methylbutene-1	0.042	0.012	71	0.026	0.006	77
Average			62			73
Internally bonded olefins						
c-Butene-2	0.006	0.001>N[e]	>83	0.006	0.001>N[e]	>83
t-Butene-2	0.007	0.001>N	>86	0.007	0.001>N	>86
c-Pentene-2	0.030	0.003	90	0.019	0.001>N	>95
t-Pentene-2	0.050	0.005	90	0.039	0.001>N	>97
2-Methylbutene-2	0.107	0.002	98	0.078	0.001>N	>99
Average			96			>97[f]
C_4 + Olefins[d]	1.81 µg	0.40	78	1.86 µg	0.41	78
Paraffins						
Isobutane	0.020	0.18	10	0.015	0.013	13
n-Butane	0.154	0.132	14	0.115	0.111	3
Isopentane	0.191	0.167	13	0.143	0.128	10
n-Pentane	0.066	0.058	12	0.051	0.046	10
Average			12			9

[a]Average values for two or more runs.
[b]Chamber concentration before irradiation.
[c]Chamber concentration after two average residence times.
[d]Olefins determined by wet chemical analysis (6); results in micrograms per liter.
[e]Values are less than stated value, which is limit of detection.
[f]Average value is estimated; actual value is not determinable because of limit of detection.

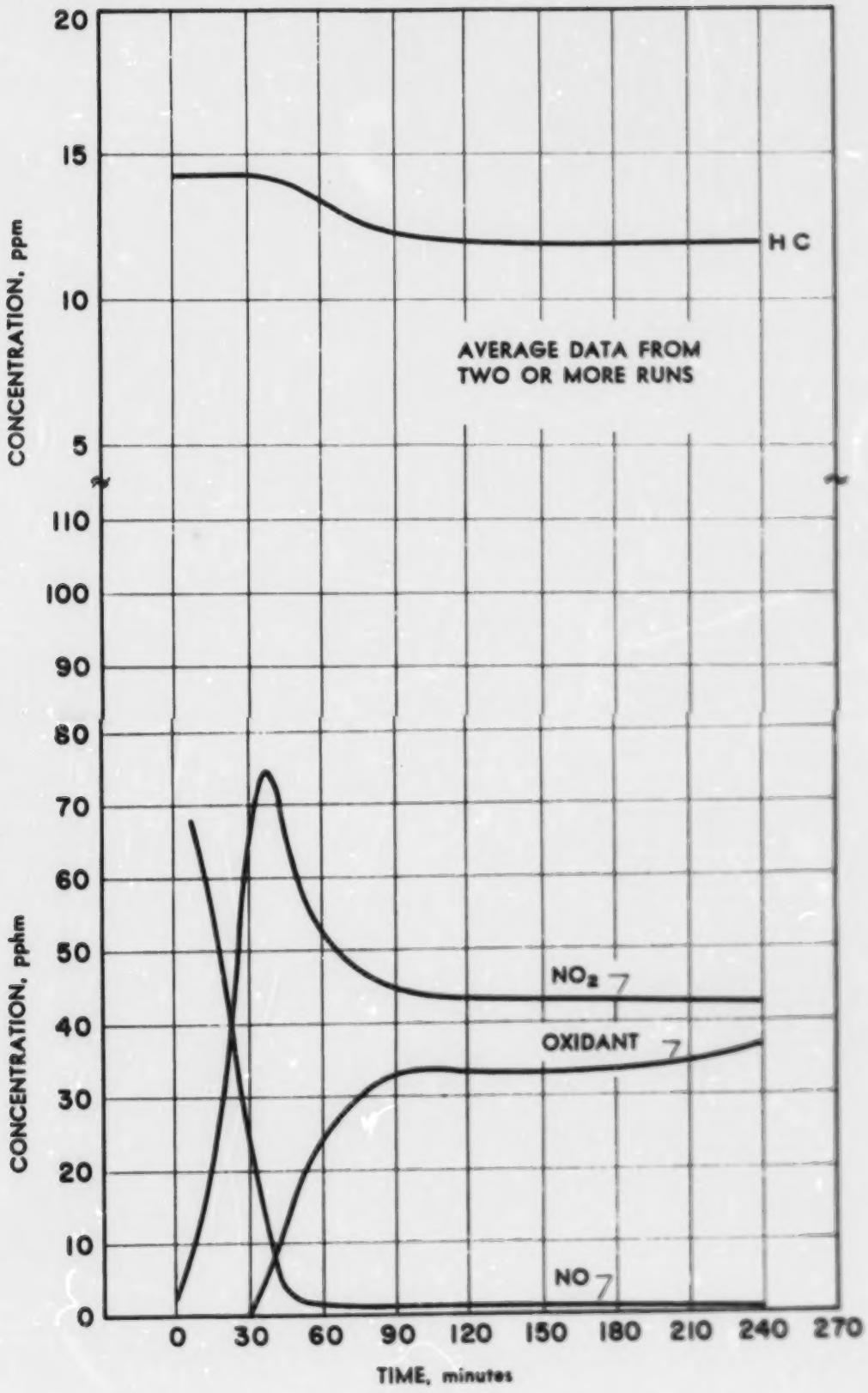


Figure A1. Test conditions: atmospheric level, 85-minute AIT, fuel no. 3

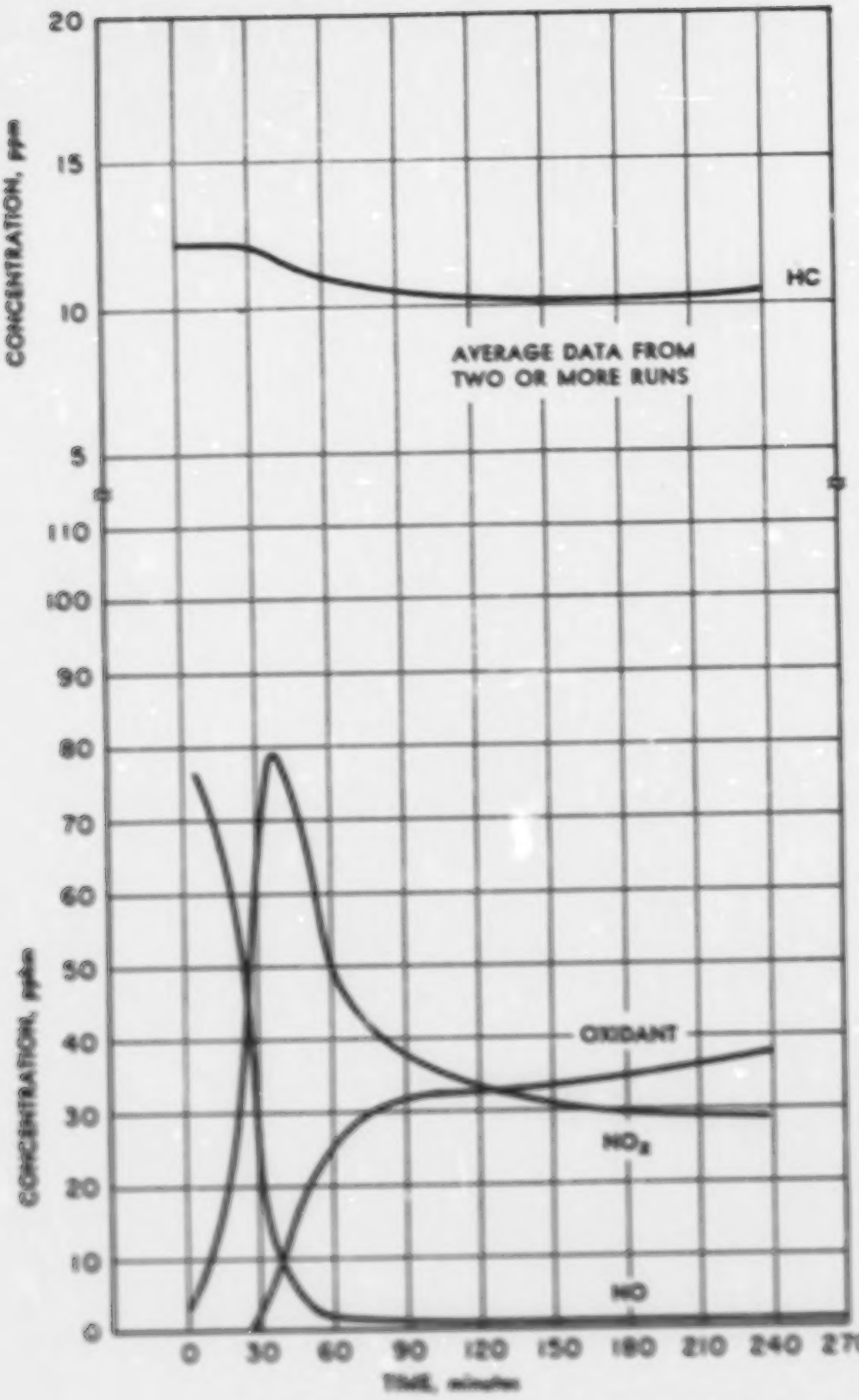


Figure A2. Test conditions: atmospheric level, 120-minute AIT, fuel no. 3

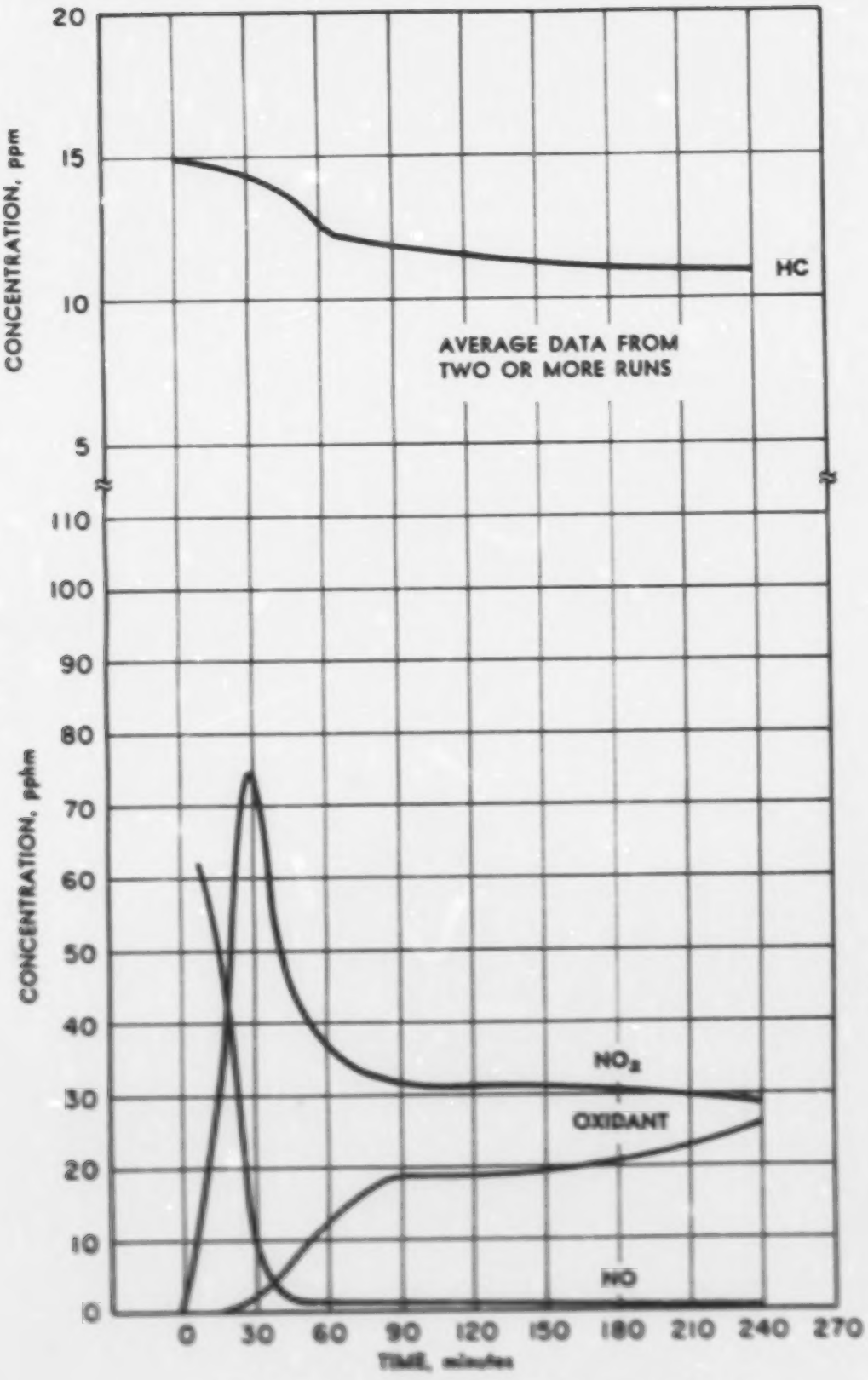


Figure A3. Test conditions: atmospheric level, 85-minute AIT, fuel no. 5

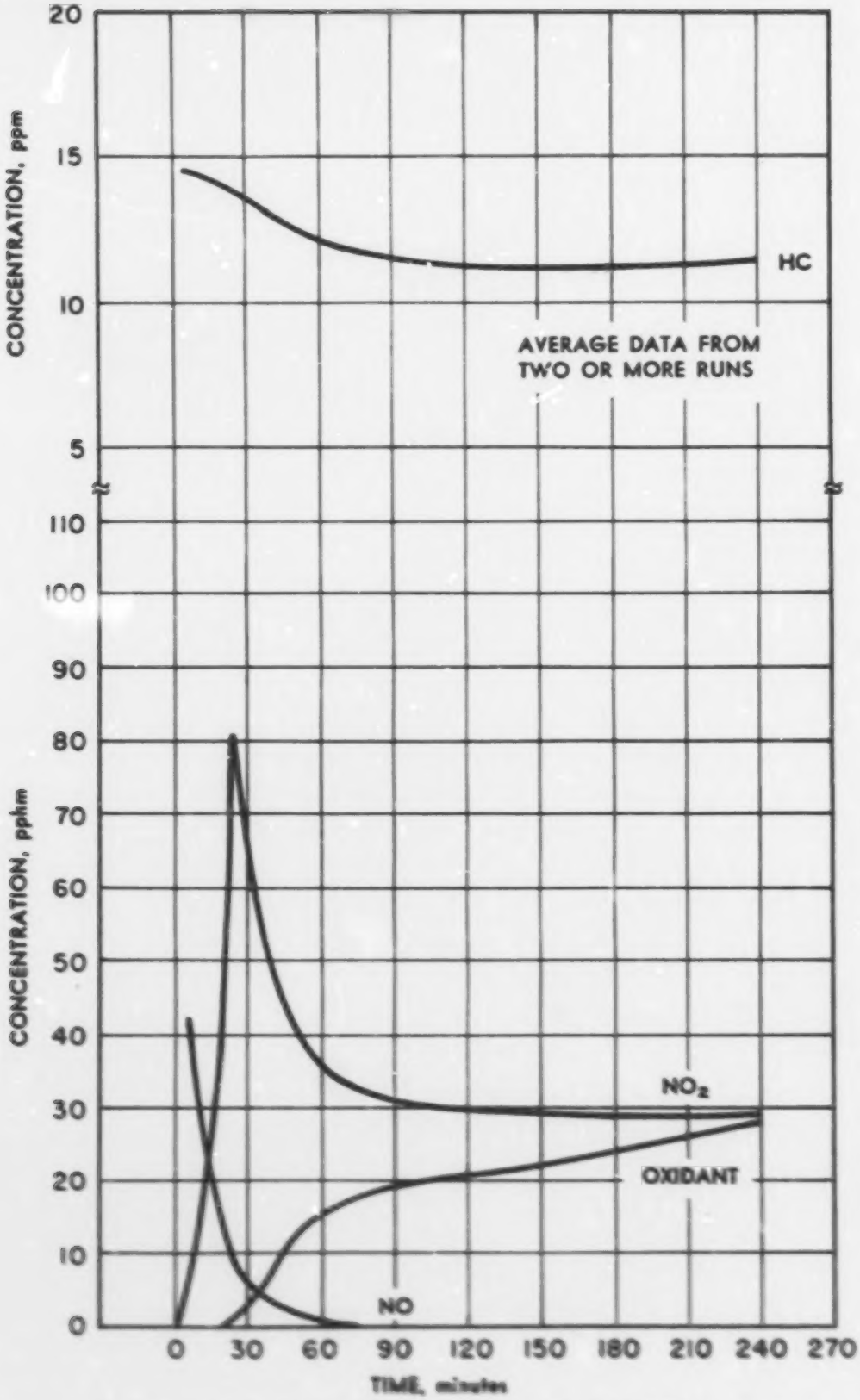


Figure A4. Test conditions: atmospheric level, 120-minute AIT, fuel no. 5

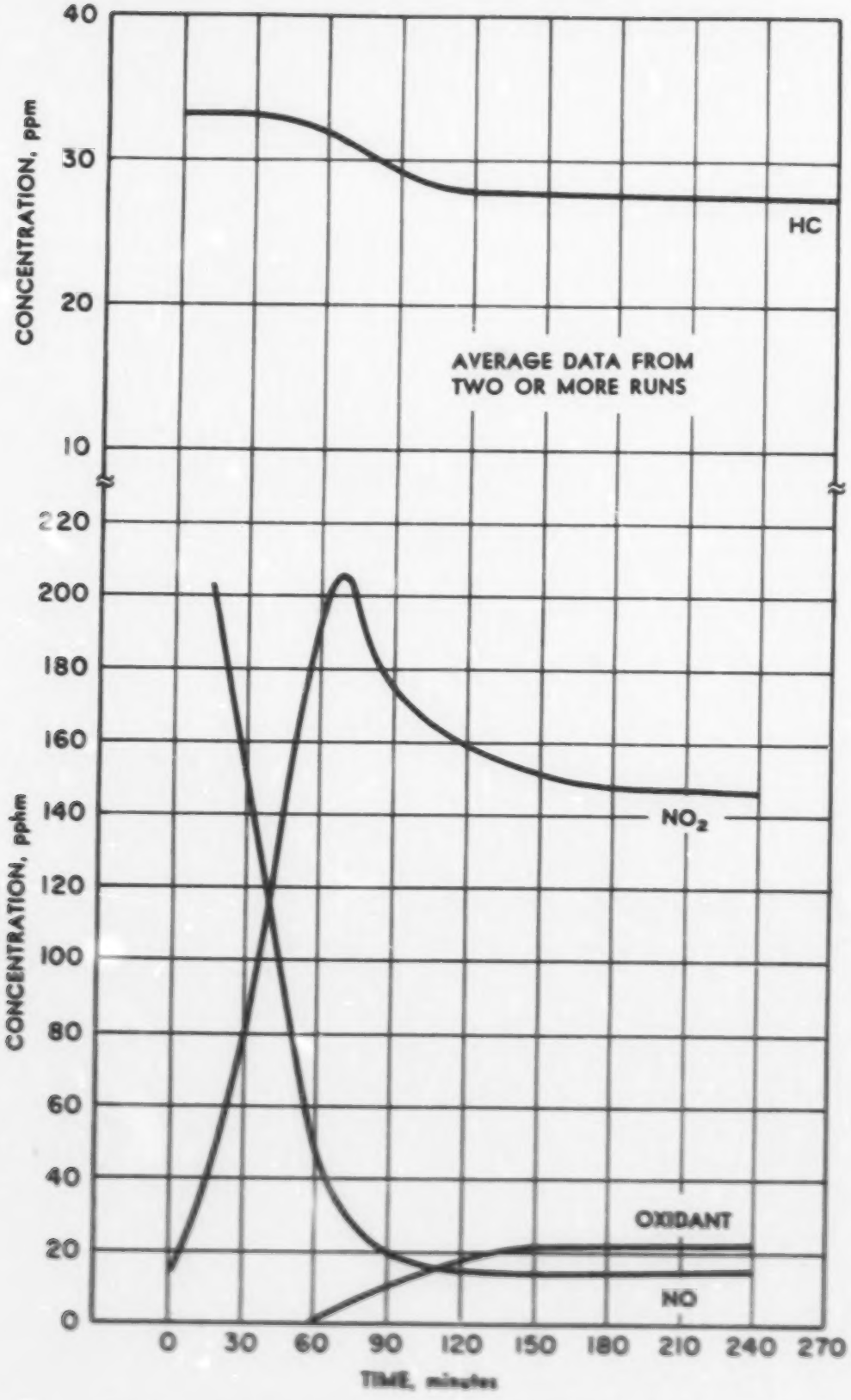


Figure A5. Test conditions: concentrated level, 85-minute AIT, fuel no. 3

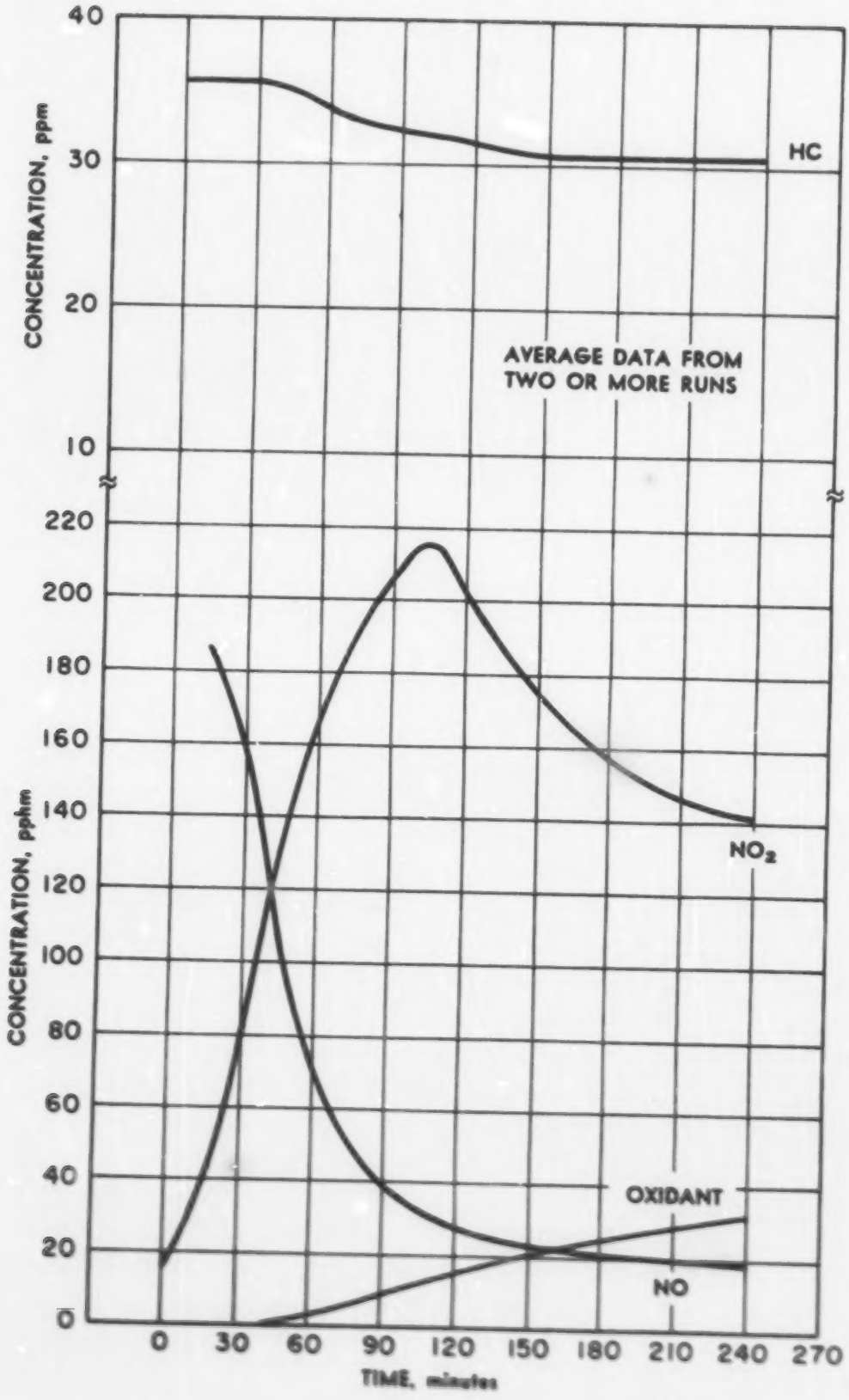


Figure A6. Test conditions: concentrated level, 120-minute AIT, fuel no. 3

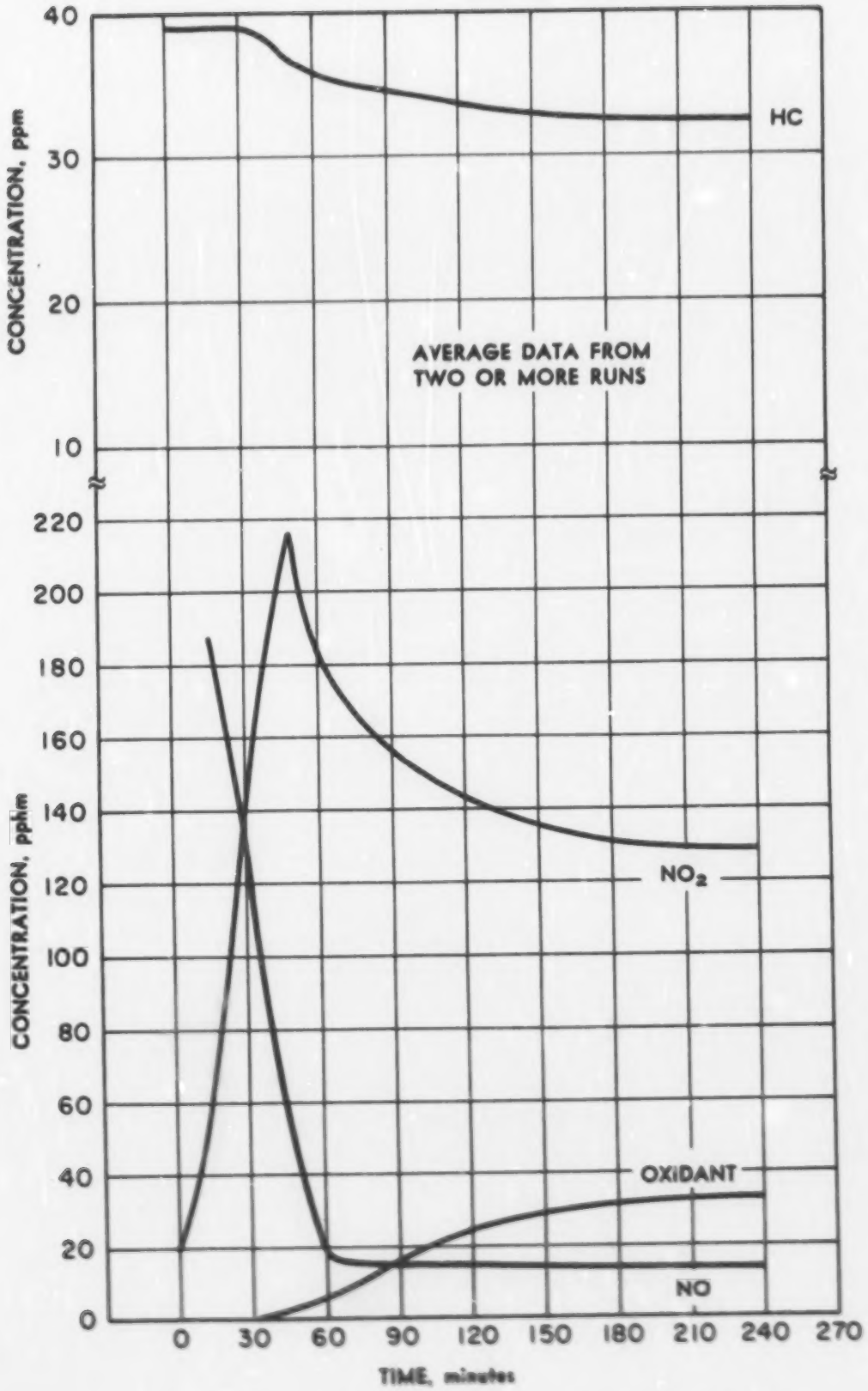


Figure A7. Test conditions: concentrated level, 85-minute AIT, fuel no. 5

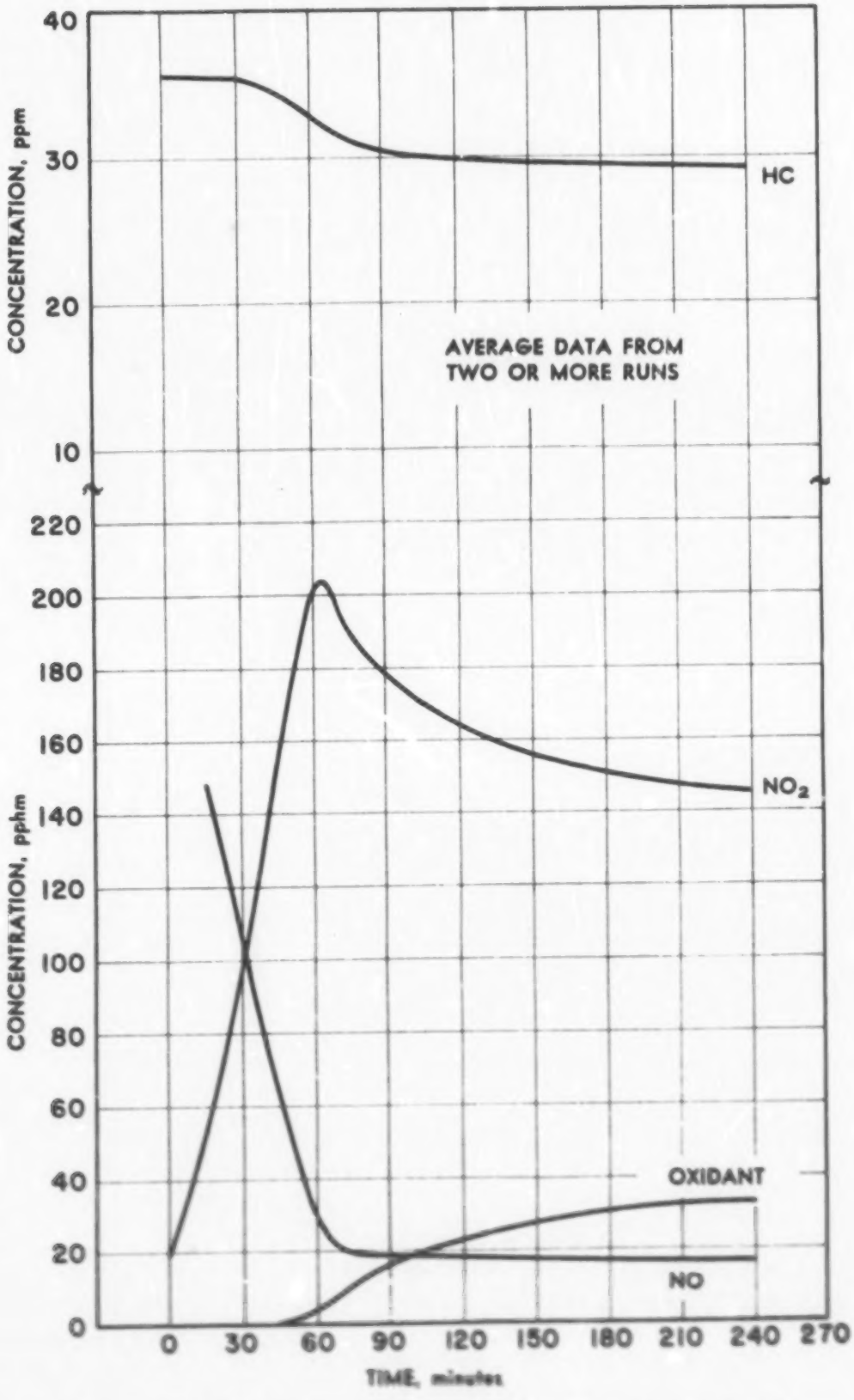


Figure A8. Test conditions: concentrated level, 120-minute AIT, fuel no. 5

APPENDIX B

COMPUTER PROGRAM FOR REDUCTION OF OXIDES OF NITROGEN DATA

COMPUTER PROGRAM FOR REDUCTION OF OXIDES OF NITROGEN DATA

The Borman colorimetric instrument used to measure nitric oxide and nitrogen dioxide has a very slow time response. The concentration indicated at any particular time is a value averaged over a considerable period of time, since the deadtime is 4 minutes and the time constant ranges from 9 to 22 minutes over the concentration range of interest. This large time constant produces extreme "tailing" or "lagging" of the indicated concentration behind the actual concentration of the gas being sampled. For adjusting the observed concentration to true or instantaneous concentrations at the designated times, a computational procedure was developed for the IBM 650 computer.

In general the operation of instruments and other dynamic systems may be described as:

(Output Function) = (Input Function) (System Function)

If the system function for a particular instrument can be defined, it is possible to compute the input function from the output function.

The system function for the Borman instrument was determined experimentally as being $(1-e^{-kt})$ where "t" = time and "k" is a constant for any given concentration.

Therefore: Output = Input $(1-e^{-kt})$.

This equation was evaluated experimentally by observing the response of the instrument as the concentration of NO or NO_2 diluted in nitrogen was switched abruptly from zero to various levels ranging from 0.25 to 2.0 ppm and from these levels back to zero. Samples of NO and NO_2 in nitrogen were prepared in Mylar bags. This procedure introduces a step input to the instrument and produces an output from which the exponent can be determined and the equation validated.

On the basis of LaPlace transforms, the exponential $(1-e^{-kt})$ is equivalent to the differential expression:

$$\left(\frac{1}{Ts+1}\right)$$

Where T is the time constant function, $f\ (\frac{1}{k})$, and s is the differential operator (d/dt). In this form the system function is usually called the transfer function. If the output concentration is termed Y and the input concentration is termed X, the equation becomes:

$$Y = X\left(\frac{1}{Ts + 1}\right)$$

which reduces to

$$Y + T\,\frac{dy}{dt} = X$$

This differential equation is solved by the computer to adjust the oxides of nitrogen data at 3-minute intervals. The time constant function, T, is a variable that is dependent upon the output concentration Y. This relationship, determined experimentally as previously described, is stored in the computer. The coefficients of this function must, of course, be determined each time the instrument is modified or a different instrument is used.

COMPUTER PROGRAM
FOR
DATA REDUCTION

INPUT CONSTANTS

1) t_o
2) Δt
3) dt_{NO}
4) dt_{NO_2}
5) t_{max}
6) t_{lts}

INPUT FUNCTIONS

1) $Y_{NO} = f(t)$, Univariate table, up to 200 points (Linear Interpolation)
2) $Y_{NO_2} = f(t)$, Univariate table, up to 200 points (Linear Interpolation

3) $T_{NO^+} = f(Y_{NO})$
4) $T_{NO^-} = f(Y_{NO})$
5) $T_{NO_2^+} = f(Y_{NO_2})$
6) $T_{NO_2^-} = f(Y_{NO_2})$

Table or equation, whichever is more convenient for computer programmer. Equation constants must be adjustable.

7) $PPM_{NO} = f(X_{NO})$
8) $PPM_{NO_2} = f(X_{NO_2})$

OUTPUT

1) t_L
2) t_{NO}
3) t_{NO_2}
4) PPM_{NO}
5) PPM_{NO_2}
6) X_{NO}
7) X_{NO_2}

Additional printout of constants involved in curve fits, etc. should be printed once for each case.

PROCEDURE

1) Read Program
2) Read Input
3) $t = t_o$
4) $Y_{NO} = f(t)$, Tabular input function
5) $Y_{NO_2} = f(t)$, Tabular input function

6) $$\left(\frac{dy}{dt}\right)_{NO} = \frac{\frac{Y_{NO+1} - Y_{NO}}{{}^{t}Y_{NO+1} - {}^{t}Y_{NO}} + \frac{Y_{NO} - Y_{NO-1}}{{}^{t}Y_{NO} - {}^{t}Y_{NO-1}}}{2}$$

7) $$\left(\frac{dy}{dt}\right)_{NO_2} = \frac{\frac{Y_{NO_2+1} - Y_{NO_2}}{{}^{t}Y_{NO_2+1} - {}^{t}Y_{NO_2}} + \frac{Y_{NO_2} - Y_{NO_2-1}}{{}^{t}Y_{NO_2} - {}^{t}Y_{NO_2-1}}}{2}$$

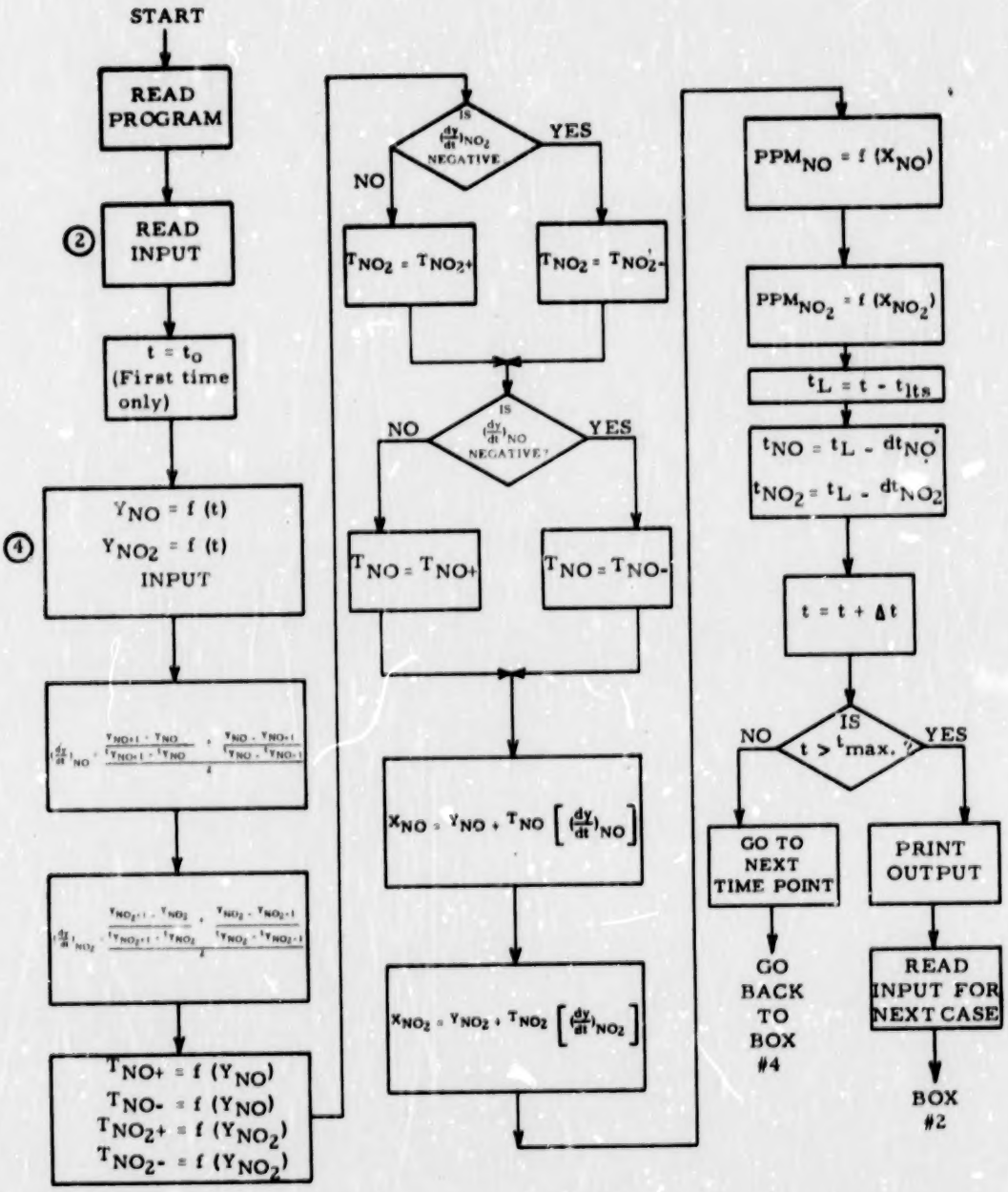
8) $T_{NO^+} = f(Y_{NO})$
9) $T_{NO^-} = f(Y_{NO})$
10) $T_{NO_2^+} = f(Y_{NO_2})$
11) $T_{NO_2^-} = f(Y_{NO_2})$
12) (Is $\left(\frac{dy}{dt}\right)_{NO_2}$ negative?) Yes ⟶ 14; No ⟶ 13
13) $T_{NO_2} = T_{NO_2^+}$ ⟶ 15
14) $T_{NO_2} = T_{NO_2^-}$
15) (Is $\left(\frac{dy}{dt}\right)_{NO}$ negative?) Yes ⟶ 17; No ⟶ 16
16) $T_{NO} = T_{NO^+}$ ⟶ 18
17) $T_{NO} = T_{NO^-}$
18) $X_{NO} = Y_{NO} + T_{NO} \left[\left(\frac{dy}{dt}\right)_{NO}\right]$
19) $X_{NO_2} = Y_{NO_2} + T_{NO_2} \left[\left(\frac{dy}{dt}\right)_{NO_2}\right]$
20) $PPM_{NO} = f(X_{NO})$
21) $PPM_{NO_2} = f(X_{NO_2})$
21A) $t_L = t - t_{lts}$
22) $t_{NO} = t_L - dt_{NO}$
23) $t_{NO_2} = t_L - dt_{NO_2}$
24) $t = t + \Delta t$
25) Is $t > t_{max.}$? Yes ⟶ 26; No ⟶ 4
26) Print Output
27) Go to 2, read next case.

NOMENCLATURE

t_o	-	Time that instrument was put on stream (minutes).
Δt	-	Time increment at which output is to be printed (minutes).
dt_{NO}	-	Deadtime for NO function.
dt_{NO_2}	-	Deadtime for NO_2 function.
t_{max}	-	Last time value for input functions Y_{NO} and Y_{NO_2} (minutes).
Y_{NO}	-	Chart indication for NO.
Y_{NO+1}	-	Chart indication for NO at next time point.

Y_{NO-1}	-	Chart indication for NO at preceding time point.
Y_{NO_2}	-	Chart indication for NO_2.
$(\frac{dy}{dt})_{NO}$	-	Average slope of Y_{NO} function at this time point.
$(\frac{dy}{dt})_{NO_2}$	-	Average slope of Y_{NO_2} function at this time point.
T_{NO^+}	-	Time constant for NO function for positive slopes.
T_{NO^-}	-	Time constant for NO function for negative slopes.
T_{NO_2+}	-	Time constant for NO_2 function for positive slopes.
T_{NO_2-}	-	Time constant for NO_2 function for negative slopes.
T_{NO}	-	Time constant used for NO computation.
T_{NO_2}	-	Time constant used for NO_2 computation.
X_{NO}	-	Adjusted NO chart indication.
X_{NO_2}	-	Adjusted NO_2 chart indication.
PPM_{NO}	-	Parts per million NO.
PPM_{NO_2}	-	Parts per million NO_2.
t_{NO}	-	Time for NO function after deadtime correction.
t_{NO_2}	-	Time for NO_2 function after deadtime correction.
t_{lts}	-	Time after t_o that lights were turned on.

BLOCK DIAGRAM



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